

TABLE OF CONTENTS

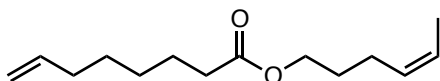
General Information.....	S2
Synthesis of diene substrates 6 – 12	S2
General procedure for catalyst initiation experiments.....	S6
Synthesis of macrocycles Z-6 – Z-12	S6
Synthesis of <i>E/Z</i> macrocycles.....	S9
References.....	S11
NMR Data.....	S12

General Information

Unless otherwise specified, all manipulations were carried out under air-free conditions in dry glassware in a Vacuum Atmospheres Glovebox filled with N₂. General solvents were purified by passing through solvent purification columns. Commercially available substrates were used as received. All solvents and substrates were sparged with Ar before bringing into the glovebox and filtered over neutral alumina (Brockmann I) prior to use. **5** was synthesized according to literature procedure.¹ **4** was provided by Materia, Inc.

Kinetic NMR experiments were performed on a Varian 600 MHz spectrometer with an AutoX probe. Spectra were analyzed using MestReNova Ver. 8.1.2. ¹H and ¹³C NMR characterization data were obtained on a Bruker 400 with Prodigy broadband cryoprobe and referenced to residual protio-solvent.

Synthesis of (Z)-hex-4-en-1-yl oct-7-enoate (**6**)



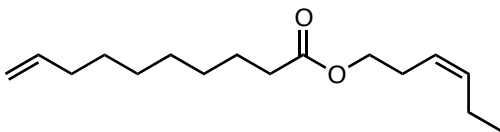
To a 100 mL round-bottom flask charged with a stir bar were added 50 mL dichloromethane, 7-octenoic acid (1.54 mL, 10.0 mmol) and pyridine (80.7 μ L, 1.00 mmol). Oxalyl chloride (1.00 mL, 11.8 mmol) was added dropwise, and the reaction was stirred overnight. Solvents were then removed *in vacuo*. 20 mL dichloromethane and pyridine (0.81 mL, 10.0 mmol) were added, and *cis*-4-hexenol (1.09 mL, 9.3 mmol) was subsequently added dropwise at 0 °C. After bringing the reaction to room temperature, it was stirred for an additional 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and sat. aq. NaHCO₃ (200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et₂O: pentane) to yield a colorless oil (1.58 g, 76% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.49 (dddd, *J* = 10.7, 8.2, 6.7, 5.2 Hz, 1H), 5.42 - 5.29 (m, 1H), 4.99 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.16 - 1.98 (m, 4H), 1.73 - 1.55 (m, 7H), 1.46 - 1.28 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 174.00, 138.94, 129.24, 125.03, 114.53, 63.89, 34.45, 33.70, 28.74, 28.66, 28.56, 24.98, 23.31, 12.85.

HRMS (FAB⁺): [M]⁺ C₁₄H₂₄O₂ Calculated – 224.1776, Found – 224.1745.

Synthesis of (Z)-hex-3-en-1-yl dec-9-enoate (**7**)



To a 100 mL round-bottom flask charged with a stir bar were added 50 mL dichloromethane, 9-decenoic acid (1.85 mL, 10.0 mmol) and pyridine (80.7 μ L, 1.00 mmol). Oxalyl chloride (1.00 mL, 11.8 mmol) was added dropwise, and the reaction was

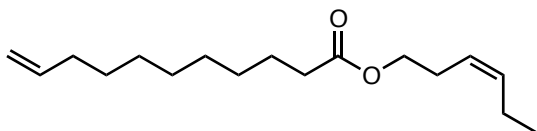
stirred overnight. Solvents were then removed *in vacuo*. 20 mL dichloromethane and pyridine (0.81 mL, 10.0 mmol) were added, and *cis*-3-hexenol (1.10 mL, 9.3 mmol) was subsequently added dropwise at 0 °C. After bringing the reaction to room temperature, it was stirred for an additional 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and sat. aq. NaHCO₃ (200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et₂O: pentane) to yield a colorless oil (2.02 g, 86% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.64 – 5.37 (m, 1H), 5.37 – 5.14 (m, 1H), 5.02 – 4.94 (m, 1H), 4.92 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.05 (t, *J* = 6.9 Hz, 2H), 2.43 – 2.32 (m, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.12 – 1.89 (m, 4H), 1.67 – 1.50 (m, 2H), 1.42 – 1.19 (m, 8H), 0.96 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.01, 139.22, 134.61, 123.90, 114.31, 63.88, 34.46, 33.89, 29.23, 29.21, 29.04, 28.97, 26.89, 25.07, 20.73, 14.37.

HRMS (FAB⁺): [M]⁺ C₁₇H₃₀O₂ Calculated – 266.2246, Found – 266.2216.

Synthesis of (*Z*)-hex-3-en-1-yl undec-10-enoate (8)



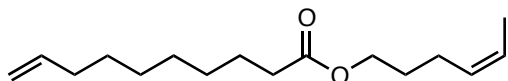
To a 100 mL round-bottom flask charged with a stir bar were added 20 mL dichloromethane, undecenoyl chloride (2.37 mL, 11.0 mmol), and pyridine (0.89 mL, 11.0 mmol). *Cis*-3-hexenol (1.18 mL, 10.0 mmol) was then added dropwise at 0 °C. The reaction mixture was brought to room temperature and stirred for 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and sat. aq. NaHCO₃ (200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et₂O: pentane) to yield a colorless oil (2.53 g, 95% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.55 – 5.45 (m, 1H), 5.36 – 5.26 (m, 1H), 4.99 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.92 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.06 (t, *J* = 6.9 Hz, 2H), 2.43 – 2.31 (m, 2H), 2.32 – 2.24 (m, 2H), 2.04 (dddd, *J* = 14.8, 7.9, 5.0, 1.5 Hz, 4H), 1.67 – 1.54 (m, 2H), 1.42 – 1.33 (m, 2H), 1.33 – 1.24 (m, 8H), 0.97 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.06, 139.32, 134.63, 123.92, 114.28, 63.89, 34.49, 33.94, 29.43, 29.35, 29.26, 29.20, 29.04, 26.90, 25.11, 20.75, 14.39.

HRMS (FAB⁺): [M]⁺ C₁₇H₃₀O₂ Calculated – 266.2246, Found – 266.2216.

Synthesis of (Z)-hex-4-en-1-yl dec-9-enoate (9)



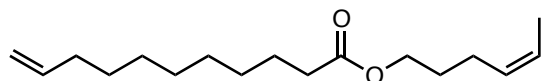
To a 100 mL round-bottom flask charged with a stir bar were added 50 mL dichloromethane, 9-decenoic acid (1.85 mL, 10.0 mmol) and pyridine (80.7 μ L, 1.00 mmol). Oxalyl chloride (1.00 mL, 11.8 mmol) was added dropwise, and the reaction was stirred overnight. Solvents were then removed *in vacuo*. 20 mL dichloromethane and pyridine (0.81 mL, 10.0 mmol) were added, and *cis*-4-hexenol (1.09 mL, 9.3 mmol) was subsequently added dropwise at 0 °C. After bringing the reaction to room temperature, it was stirred for an additional 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and sat. aq. NaHCO₃ (200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et₂O: pentane) to yield a colorless oil (2.05 g, 87% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.80 (ddt, J = 13.2, 10.0, 7.2 Hz, 1H), 5.60 - 5.44 (m, 1H), 5.44 - 5.32 (m, 1H), 5.12 - 4.96 (m, 1H), 4.93 (ddd, J = 10.2, 2.3, 1.2 Hz, 1H), 4.07 (t, J = 6.5 Hz, 2H), 2.30 (t, J = 8.0 Hz, 2H), 2.20 - 1.96 (m, 4H), 1.81 - 1.58 (m, 7H), 1.49 - 1.24 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 174.12, 139.29, 129.27, 125.05, 114.34, 63.89, 34.53, 33.92, 29.26, 29.07, 29.00, 28.59, 25.14, 23.34, 12.88.

HRMS (FAB+): [M+H] C₁₆H₂₉O₂ Calculated – 253.2158, Found – 253.2168.

Synthesis of (Z)-hex-4-en-1-yl undec-10-enoate (10)



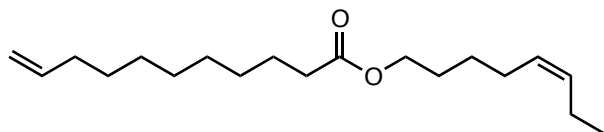
To a 100 mL round-bottom flask charged with a stir bar were added 20 mL dichloromethane, undecenoyl chloride (2.37 mL, 11.0 mmol), and pyridine (0.89 mL, 11.0 mmol). *Cis*-4-hexenol (1.17 mL, 10.0 mmol) was then added dropwise at 0 °C. The reaction mixture was brought to room temperature and stirred for 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and sat. aq. NaHCO₃ (200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et₂O: pentane) to yield a colorless oil (2.45 g, 92% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.49 (dddd, J = 10.7, 8.2, 6.7, 5.2 Hz, 1H), 5.36 (dtq, J = 10.7, 7.3, 1.7 Hz, 1H), 4.99 (dq, J = 17.2, 1.8 Hz, 1H), 4.92 (ddt, J = 10.2, 2.3, 1.2 Hz, 1H), 4.06 (t, J = 6.6 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 2.11 (qt, J = 7.2, 1.2 Hz, 2H), 2.07 – 1.99 (m, 2H), 1.73 – 1.64 (m, 2H), 1.60 (ddt, J = 6.7, 1.8, 0.9 Hz, 6H), 1.36 (dt, J = 8.3, 4.8 Hz, 2H), 1.28 (q, J = 4.1, 3.3 Hz, 7H).

¹³C NMR (101 MHz, CDCl₃) δ 174.12, 139.33, 129.26, 125.04, 114.28, 63.89, 34.54, 33.94, 29.44, 29.36, 29.28, 29.21, 29.04, 28.58, 25.15, 23.33, 12.86.

HRMS (FAB+): [M+H] C₁₇H₃₁O₂ Calculated – 267.2324, Found – 267.2335.

Synthesis of (Z)-oct-5-en-1-yl undec-10-enoate (11)



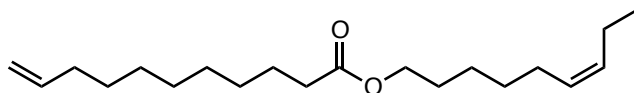
To a 100 mL round-bottom flask charged with a stir bar were added 20 mL dichloromethane, undecenoyl chloride (2.37 mL, 11.0 mmol), and pyridine (0.89 mL, 11.0 mmol). *Cis*-5-octenol (1.51 mL, 10.0 mmol) was then added dropwise at 0 °C. the reaction mixture was brought to room temperature and stirred for 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and sat. aq. NaHCO₃ (200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et₂O: pentane) to yield a colorless oil (2.82 g, 96% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.82 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.46 - 5.37 (m, 1H), 5.36 - 5.25 (m, 1H), 5.01 (dq, *J* = 17.1, 1.8 Hz, 1H), 4.94 (ddt, *J* = 10.2, 2.4, 1.2 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 2.06 (dddd, *J* = 10.9, 9.5, 5.3, 1.6 Hz, 6H), 1.72 - 1.61 (m, 4H), 1.47 - 1.27 (m, 12H), 0.97 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.99, 139.17, 132.16, 128.49, 114.14, 64.22, 34.39, 33.80, 29.31, 29.22, 29.14, 29.07, 28.90, 28.23, 26.63, 26.05, 25.02, 20.54, 14.36.

HRMS (FAB⁺): [M+H] C₁₉H₃₅O₂ Calculated – 295.2637, Found – 295.2639.

Synthesis (Z)-non-6-en-1-yl undec-10-enoate (12)



To a 100 mL round-bottom flask charged with a stir bar were added 20 mL dichloromethane, undecenoyl chloride (2.37 mL, 11.0 mmol), and pyridine (0.89 mL, 11.0 mmol). *Cis*-6-nonenol (1.67 mL, 10.0 mmol) was then added dropwise at 0 °C. The reaction mixture was brought to room temperature and stirred for 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and sat. aq. NaHCO₃ (200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et₂O: pentane) to yield a colorless oil (2.74 g, 89% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.50 – 5.16 (m, 2H), 5.04 – 4.94 (m, 1H), 4.94 – 4.88 (m, 1H), 4.05 (t, *J* = 6.7 Hz, 2H), 2.35 – 2.22 (m, 2H), 2.13 – 1.96 (m, 6H), 1.61 (dt, *J* = 11.8, 4.1 Hz, 4H), 1.36 (dt, *J* = 6.5, 2.2 Hz, 6H), 1.32 – 1.25 (m, 8H), 0.95 (t, *J* = 7.5 Hz, 3H).

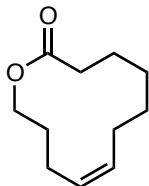
¹³C NMR (101 MHz, CDCl₃) δ 174.14, 139.32, 131.99, 128.96, 114.28, 64.47, 34.54, 33.94, 29.48, 29.44, 29.36, 29.28, 29.21, 29.03, 28.70, 27.07, 25.70, 25.15, 20.66, 14.52.

HRMS (FAB⁺): [M]⁺ C₂₀H₃₇O₂ Calculated – 309.2794, Found – 309.2779.

General Procedure for Catalyst Initiation Experiments

To an NMR tube was added a solution of catalyst (0.003 mmol) in 0.6 mL CD₂Cl₂. The tube was then sealed with a rubber septum, taken out of the glovebox, and placed in a dry ice/acetone bath. Butyl vinyl ether (12 μ L, 0.090 mmol) was injected into the tube, and the reaction was monitored by observing the disappearance of the benzyldiene signal by ¹H NMR using an array at the appropriate temperature.

Synthesis of (Z)-oxacyclododec-8-en-2-one (Z-6)



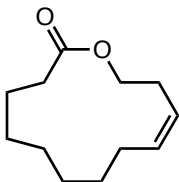
To a 150 mL Schlenk tube equipped with a stir bar were added **6** (21.0 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of **5** (4.8 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (12.0 mg, 70% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.45 - 5.21 (m, 2H), 4.10 - 3.96 (m, 2H), 2.49 - 2.28 (m, 4H), 2.18 (q, *J* = 6.3 Hz, 2H), 1.89 - 1.81 (m, 2H), 1.68 (ddq, *J* = 8.2, 4.0, 2.0 Hz, 2H), 1.47 - 1.40 (m, 2H), 1.26 - 1.18 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 174.18, 131.37, 128.57, 62.31, 35.73, 26.80, 26.30, 25.14, 24.18, 23.08, 22.42.

HRMS (FAB⁺): [M]⁺ C₁₁H₁₈O₂ Calculated – 182.1307, Found – 182.1303.

Synthesis of (Z)-oxacyclotridec-10-en-2-one (Z-7)



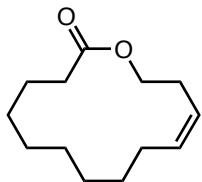
To a 150 mL Schlenk tube equipped with a stir bar was added **7** (23.7 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of **5** (4.8 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (12.5 mg, 68% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.50 - 5.32 (m, 2H), 4.30 - 4.15 (m, 2H), 2.43 (q, *J* = 5.0 Hz, 2H), 2.35 - 2.25 (m, 2H), 2.15 - 2.04 (m, 2H), 1.73 - 1.64 (m, 2H), 1.49 (q, *J* = 6.3 Hz, 2H), 1.41 - 1.33 (m, 2H), 1.22 - 1.15 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 174.89, 132.41, 127.26, 64.34, 35.54, 29.86, 27.66, 27.41, 26.15, 26.02, 24.73, 23.67.

HRMS (EI): $\text{C}_{12}\text{H}_{21}\text{O}_2$ Calculated – 197.1542, Found – 197.1536.

Synthesis of (Z)-oxacyclotetradec-11-en-2-one (Z-8)



To a 150 mL Schlenk tube equipped with a stir bar was added **8** (25.0 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of **5** (4.8 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et_2O : pentane) to yield a colorless oil (13.2 mg, 67% yield).

Large Scale Preparation:

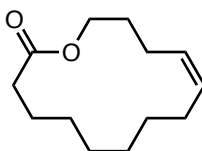
To a 500 mL Schlenk tube equipped with a stir bar was added **8** (200.0 mg, 0.750 mmol) in 246.4 mL DCM and a solution of **5** (38.4 mg, 0.0450 mmol) in 4 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 8 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et_2O : pentane) to yield a colorless oil (94.9 mg, 60% yield).

^1H NMR (400 MHz, $\text{Chloroform-}d_1$) δ 5.55 (dt, $J = 11.1, 7.7, 1.7$ Hz, 1H), 5.45 – 5.33 (m, 1H), 4.28 – 4.11 (m, 2H), 2.50 – 2.40 (m, 2H), 2.40 – 2.29 (m, 2H), 2.10 – 1.99 (m, 2H), 1.66 (ddt, $J = 6.3, 4.5, 2.5$ Hz, 2H), 1.43 – 1.30 (m, 10H).

^{13}C NMR (101 MHz, CDCl_3) δ 174.13, 132.47, 127.22, 63.89, 33.46, 27.85, 27.65, 26.25, 26.14, 25.67, 25.56, 25.34, 23.65.

HRMS (FAB+): $[\text{M}+\text{H}]$ $\text{C}_{13}\text{H}_{23}\text{O}_2$ Calculated – 211.1698, Found – 211.1706.

Synthesis of (Z)-oxacyclotetradec-10-en-2-one (Z-9)



To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **9** (23.7 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of **5** (4.8 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 1 mL butyl

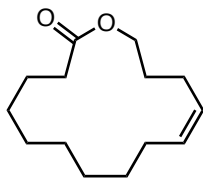
vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (14.2 mg, 72% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.48 (dt, *J* = 10.5, 7.6, 1.5 Hz, 1H), 5.33 (dt, *J* = 10.5, 7.6, 1.3 Hz, 1H), 4.22 – 4.02 (m, 2H), 2.51 – 2.37 (m, 2H), 2.25 (qd, *J* = 7.5, 1.4 Hz, 2H), 2.14 – 1.95 (m, 2H), 1.79 – 1.65 (m, 4H), 1.49 – 1.28 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 173.98, 131.23, 128.50, 62.84, 33.57, 29.11, 27.00, 26.77, 26.03, 25.23, 25.04, 24.63, 23.73.

HRMS (FAB⁺): [M+H] C₁₃H₂₃O₂ Calculated – 211.1698, Found – 211.1690.

Synthesis of (*Z*)-oxacyclopentadec-11-en-2-one (**Z-10**)



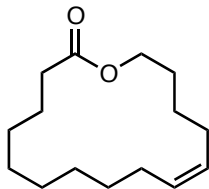
To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **10** (25.0 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of **5** (4.8 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (15.6 mg, 70% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.57 - 5.38 (m, 1H), 5.30 (dt, *J* = 10.9, 6.9 Hz, 1H), 4.18 - 3.95 (m, 2H), 2.46 - 2.32 (m, 2H), 2.23 (qd, *J* = 7.1, 1.7 Hz, 2H), 2.02 (q, *J* = 7.1 Hz, 2H), 1.72 (dtd, *J* = 8.9, 6.9, 4.3 Hz, 4H), 1.36 (dt, *J* = 8.7, 5.9 Hz, 10H).

¹³C NMR (101 MHz, CDCl₃) δ 174.45, 131.47, 128.85, 63.36, 34.51, 28.81, 28.24, 27.96, 27.12, 27.05, 27.01, 26.35, 24.63, 23.75.

HRMS (FAB⁺): [M]⁺ C₁₄H₂₄O₂ Calculated – 224.1776, Found – 224.1774.

Synthesis of (*Z*)-oxacyclohexadec-11-en-2-one (**Z-11**)



To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **11** (27.6 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of **5** (4.8 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column

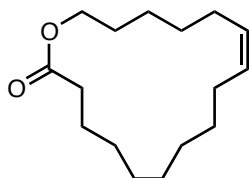
chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (17.7 mg, 79% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.53 - 5.20 (m, 2H), 4.14 (t, *J* = 6.3 Hz, 2H), 2.43 - 2.27 (m, 2H), 2.03 (qd, *J* = 7.0, 3.1 Hz, 4H), 1.63 (dq, *J* = 9.2, 6.3 Hz, 4H), 1.45 - 1.37 (m, 2H), 1.30 (q, *J* = 5.5, 4.6 Hz, 10H).

¹³C NMR (101 MHz, CDCl₃) δ 174.09, 130.24, 129.71, 64.24, 34.01, 29.28, 28.54, 28.31, 28.07, 27.76, 27.32, 27.25, 26.73, 26.61, 25.38.

HRMS (FAB+): [M+H] C₁₅H₂₇O₂ Calculated – 239.2011, Found – 239.2017.

Synthesis of (*Z*)-oxacycloheptadec-11-en-2-one (*Z*-12)



To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **12** (28.9 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of **5** (4.8 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 1 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (17.8 mg, 75% yield).

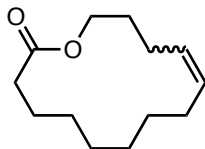
¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.39 - 5.22 (m, 2H), 4.19 - 4.01 (m, 2H), 2.38 - 2.22 (m, 2H), 2.06 (dq, *J* = 18.6, 6.1 Hz, 4H), 1.71 - 1.52 (m, 4H), 1.47 - 1.17 (m, 14H).

¹³C NMR (101 MHz, CDCl₃) δ 174.57, 130.37, 130.29, 64.75, 34.43, 29.45, 28.88, 28.84, 28.79, 28.76, 28.19, 27.73, 27.32, 26.57, 26.22, 25.57.

HRMS (FAB+): [M+H] C₁₆H₂₈O₂ Calculated – 252.2087, Found – 252.2089.

For determining selectivity, *E/Z* mixtures of lactones were synthesized using (PCy₃)₂Cl₂Ru=CHPh as references for GC and ¹³C NMR studies for comparison.

Synthesis of (*E/Z*)-oxacyclotetradec-10-en-2-one (*E/Z*-9)



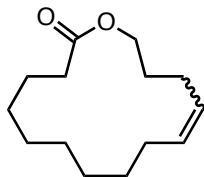
To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **9** (23.7 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of (PCy₃)₂Cl₂Ru=CHPh (4.6 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 4 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (13.0 mg, 67% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.68 - 5.42 (m, 1H), 5.42 - 5.24 (m, 1H), 4.29 - 3.98 (m, 2H), 2.53 - 2.18 (m, 4H), 2.14 - 2.05 (m, 2H), 1.79 - 1.64 (m, 4H), 1.49 - 1.20 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 174.28, 173.86, 131.11, 130.62, 130.40, 128.38, 64.81, 62.72, 33.45, 33.01, 31.42, 30.91, 28.98, 28.18, 27.06, 26.88, 26.65, 26.53, 25.91, 25.11, 24.98, 24.92, 24.51, 24.08, 23.61.

HRMS (FAB⁺): [M]⁺ C₁₃H₂₂O₂ Calculated – 210.1620, Found – 210.1633.

Synthesis of (*E/Z*)-oxacyclopentadec-11-en-2-one (*E/Z*-10)



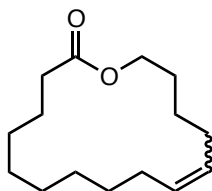
To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **10** (25.0 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of (PCy₃)₂Cl₂Ru=CHPh (4.6 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 4 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (11.7 mg, 52% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.50 - 5.20 (m, 2H), 4.19 - 4.04 (m, 2H), 2.40 - 2.29 (m, 2H), 2.20 (qd, *J* = 7.4, 6.3, 1.6 Hz, 2H), 2.09 - 1.96 (m, 2H), 1.85 - 1.54 (m, 5H), 1.45 - 1.22 (m, 11H).

¹³C NMR (101 MHz, CDCl₃) δ 174.48, 174.45, 131.97, 131.48, 129.87, 128.85, 64.30, 63.36, 35.01, 34.51, 31.02, 30.32, 28.81, 28.24, 27.96, 27.85, 27.56, 27.13, 27.05, 27.03, 27.01, 26.82, 26.63, 26.35, 25.03, 24.63, 24.57, 23.75.

HRMS (FAB⁺): [M]⁺ C₁₄H₂₄O₂ Calculated – 224.1776, Found – 224.1767.

Synthesis of (*E/Z*)-oxacyclohexadec-11-en-2-one (*E/Z*-11)



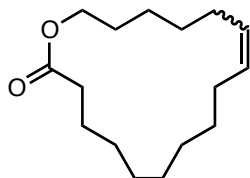
To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **11** (27.6 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of (PCy₃)₂Cl₂Ru=CHPh (4.6 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 4 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (16.8 mg, 75% yield).

¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.52 - 5.15 (m, 2H), 4.22 - 4.01 (m, 2H), 2.45 - 2.22 (m, 2H), 2.03 (ddt, *J* = 9.1, 6.8, 3.8 Hz, 4H), 1.61 (dtd, *J* = 15.7, 7.1, 4.0 Hz, 4H), 1.42 - 1.11 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 174.09, 174.07, 131.95, 130.46, 130.24, 129.71, 64.24, 64.08, 34.89, 34.01, 32.16, 32.12, 29.28, 28.54, 28.47, 28.41, 28.34, 28.31, 28.14, 28.07, 27.76, 27.34, 27.32, 27.25, 26.73, 26.68, 26.61, 25.60, 25.38, 25.30.

HRMS (FAB⁺): [M]⁺ C₁₅H₂₆O₂ Calculated – 238.1933, Found – 238.1926.

Synthesis of (*E/Z*)-oxacycloheptadec-11-en-2-one (*E/Z* -12)



To a 150 mL Schlenk tube equipped with a stir bar was added a solution of **12** (28.9 mg, 0.0938 mmol) in 30.3 mL DCM and a solution of (PCy₃)₂Cl₂Ru=CHPh (4.6 mg, 0.00563 mmol) in 1 mL DCM. The tube was sealed and taken out of the glovebox. After one freeze, pump, thaw cycle, the reaction flask was heated at 40 °C for 4 h and then quenched with 1 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified by column chromatography on silica gel (1:49 Et₂O: pentane) to yield a colorless oil (16.4 mg, 69% yield).

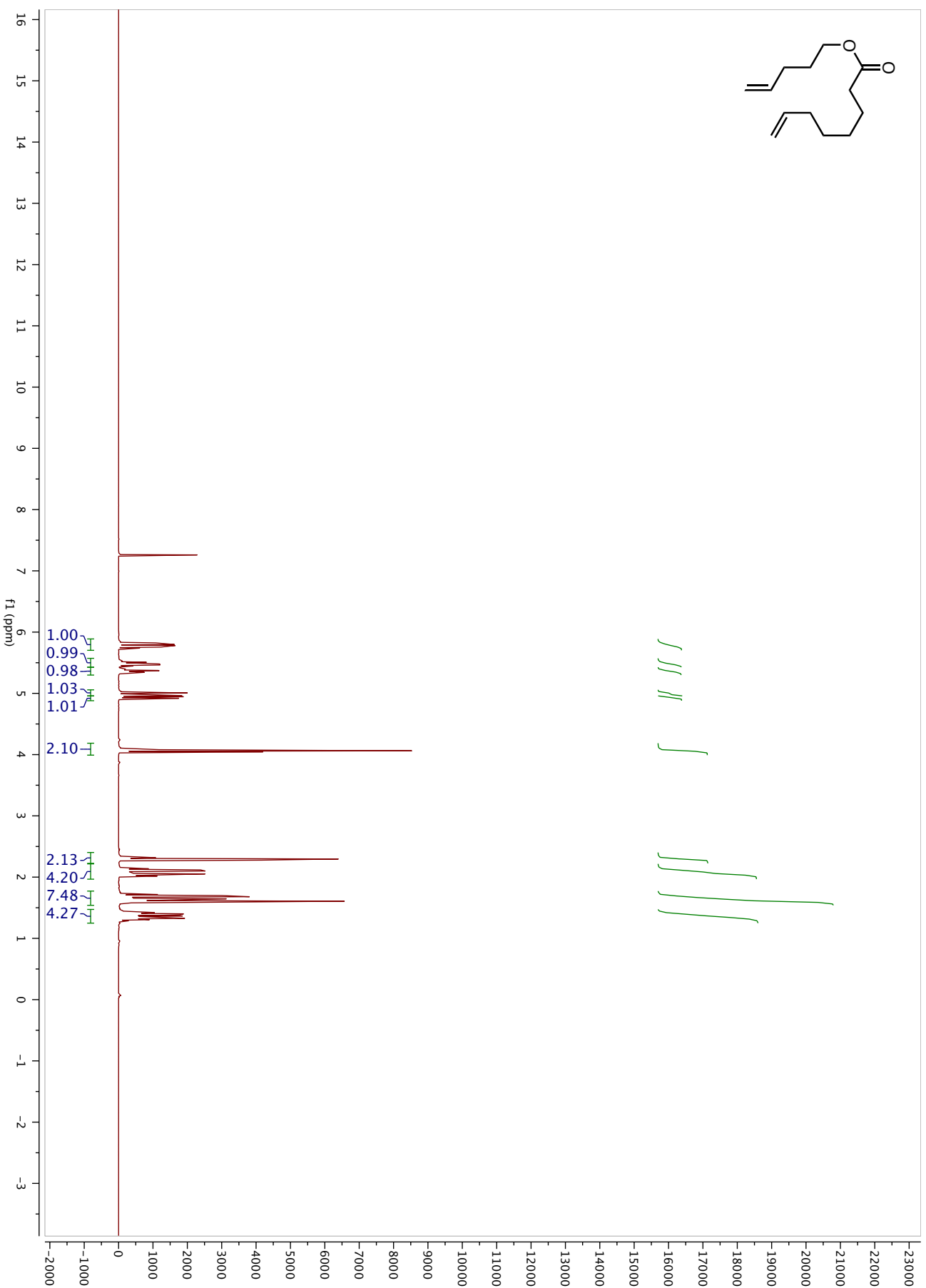
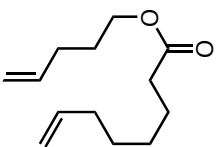
¹H NMR (400 MHz, Chloroform-*d*₁) δ 5.39 - 5.22 (m, 2H), 4.19 - 4.02 (m, 2H), 2.40 - 2.25 (m, 2H), 2.04 (ddt, *J* = 14.3, 11.9, 4.8 Hz, 4H), 1.68 - 1.56 (m, 4H), 1.48 - 1.22 (m, 14H).

¹³C NMR (101 MHz, CDCl₃) δ 173.38, 129.79, 129.71, 129.18, 129.10, 63.87, 63.56, 33.64, 33.24, 31.57, 30.70, 28.66, 28.26, 28.19, 28.14, 27.71, 27.68, 27.65, 27.60, 27.57, 27.38, 27.14, 27.00, 26.94, 26.91, 26.54, 26.13, 25.93, 25.38, 25.02, 24.96, 24.38, 24.30, 24.28.

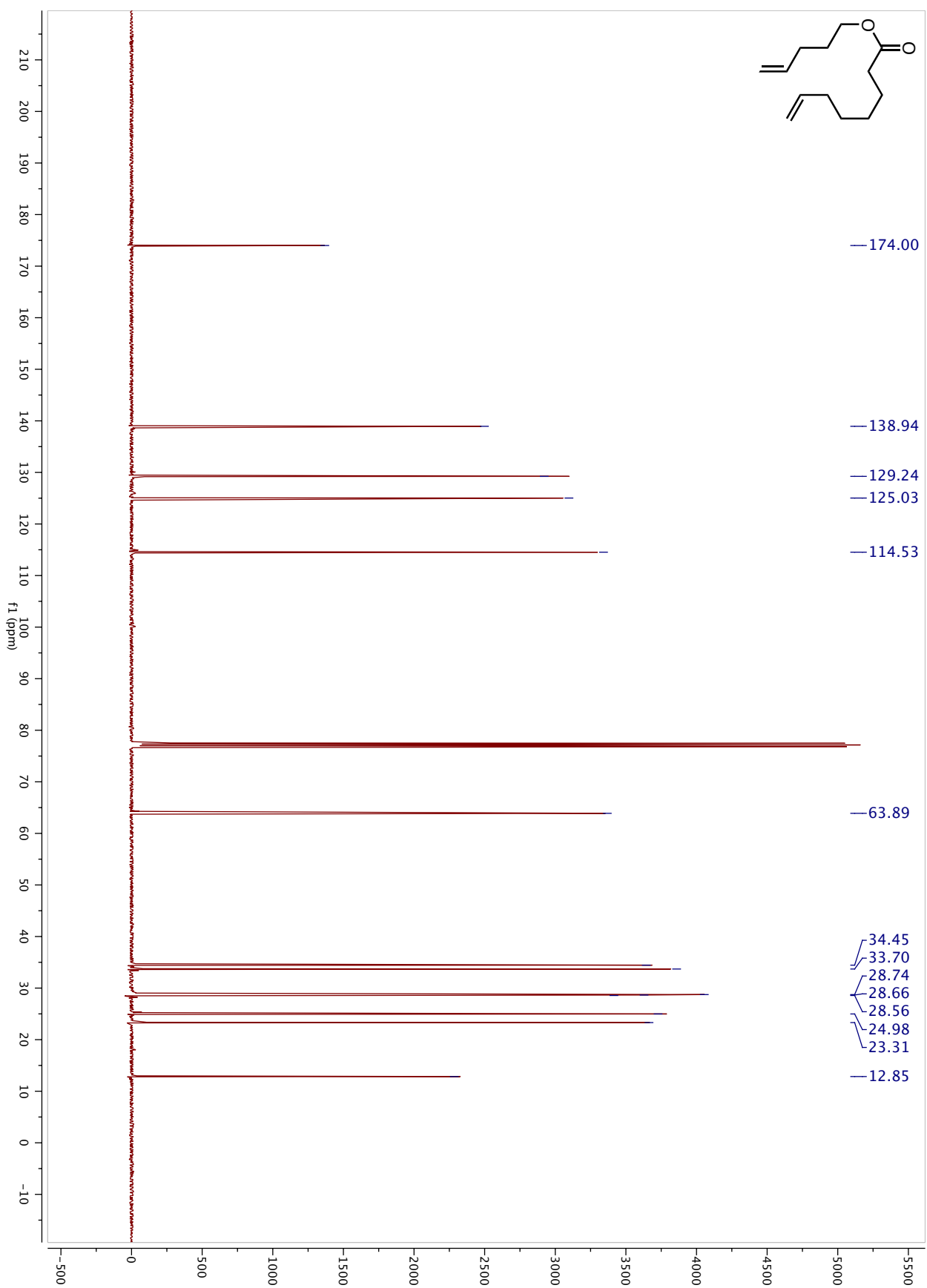
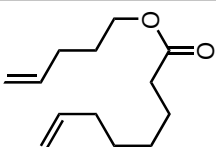
HRMS (FAB⁺): [M]⁺ C₁₆H₂₈O₂ Calculated – 252.2079, Found – 252.2089.

References

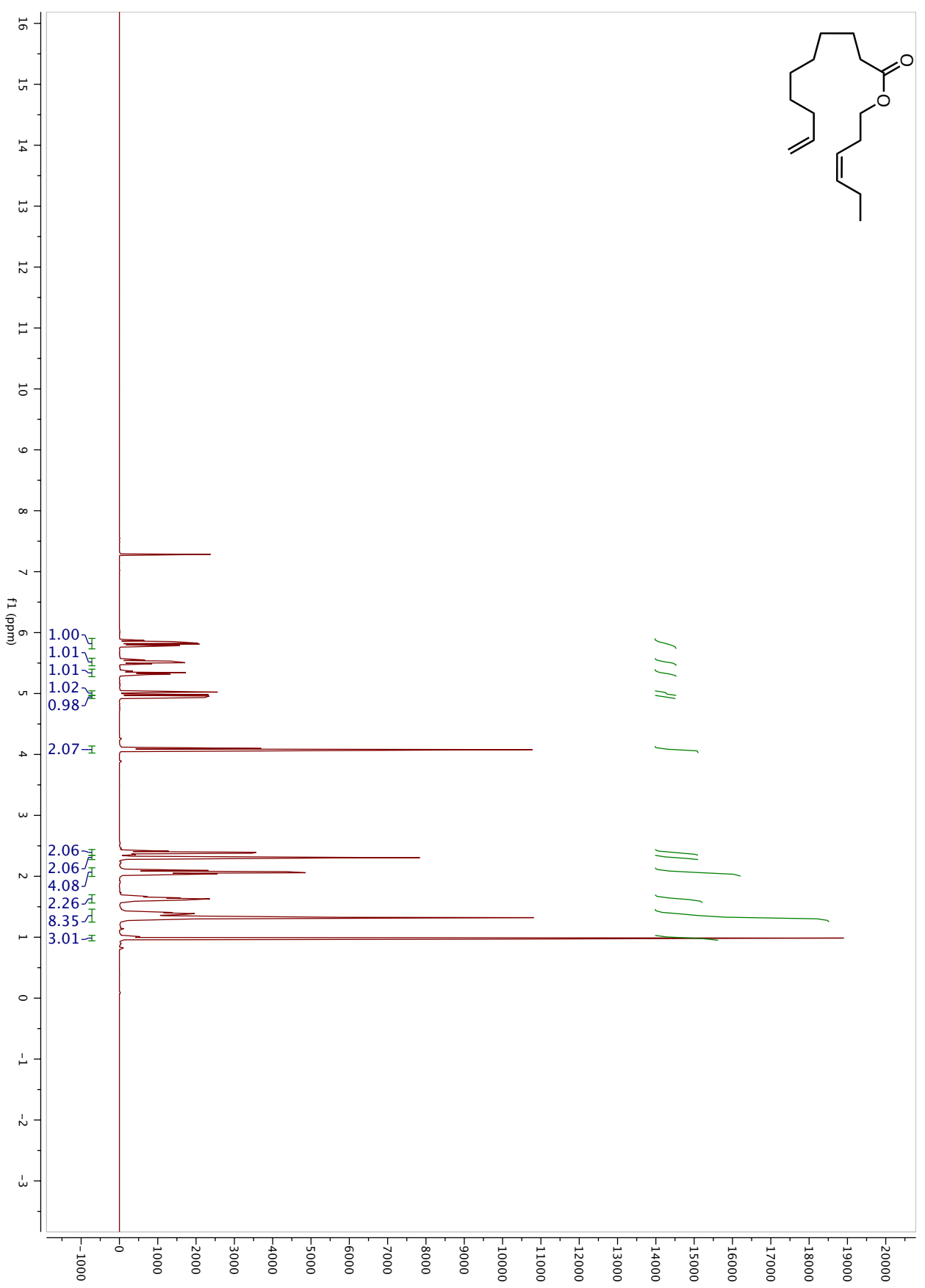
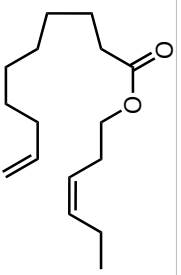
1. Johns, A. M.; Ahmed, T. S.; Jackson, B. W.; Grubbs, R. H.; Pedersen, R. L. *Org. Lett.* **2016**, *18* (4), 772.



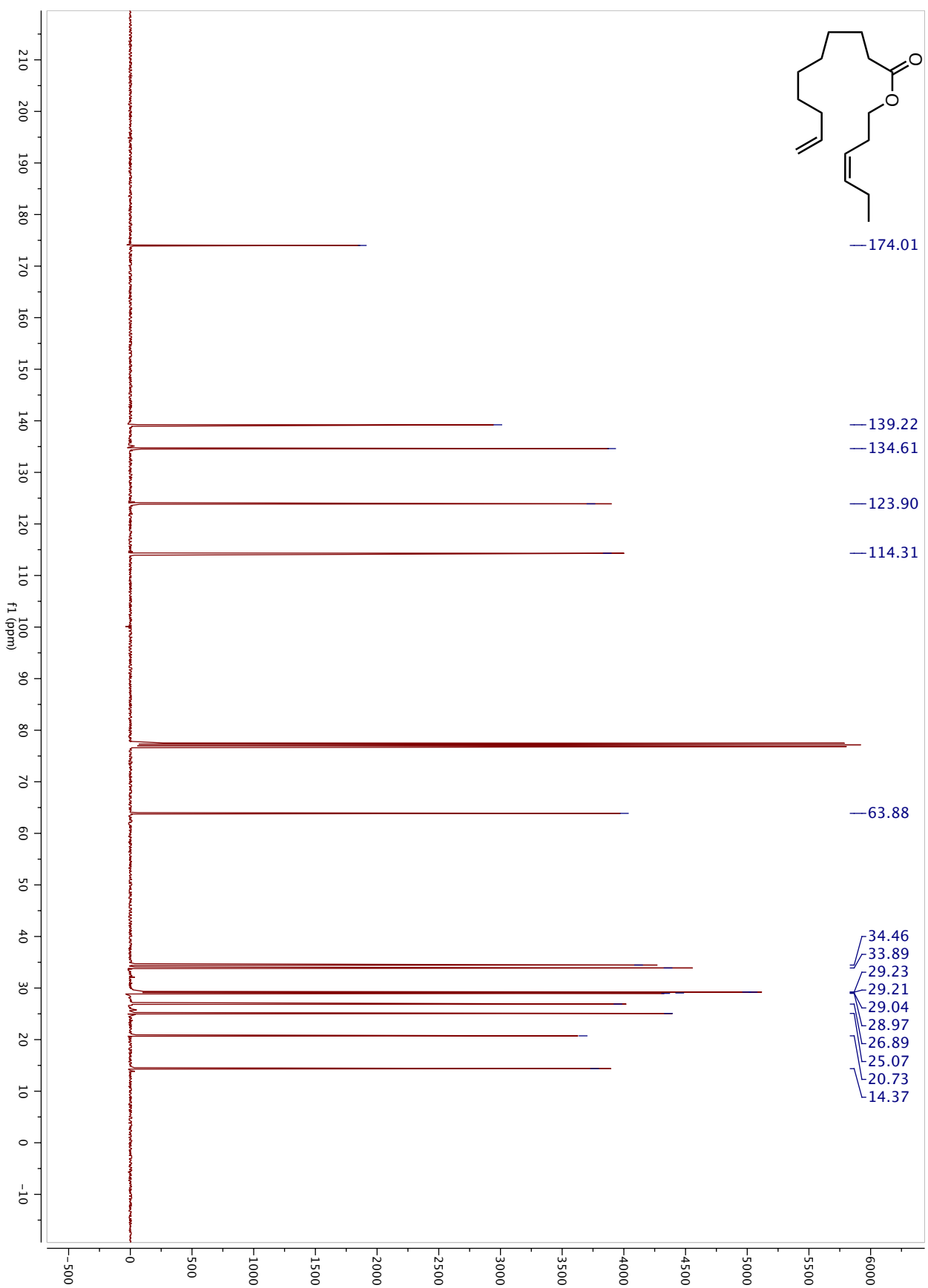
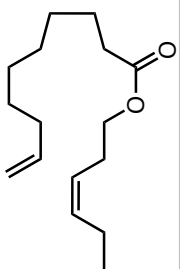
¹H NMR of (Z)-hex-4-en-1-yl oct-7-enoate (400 MHz, CDCl₃)

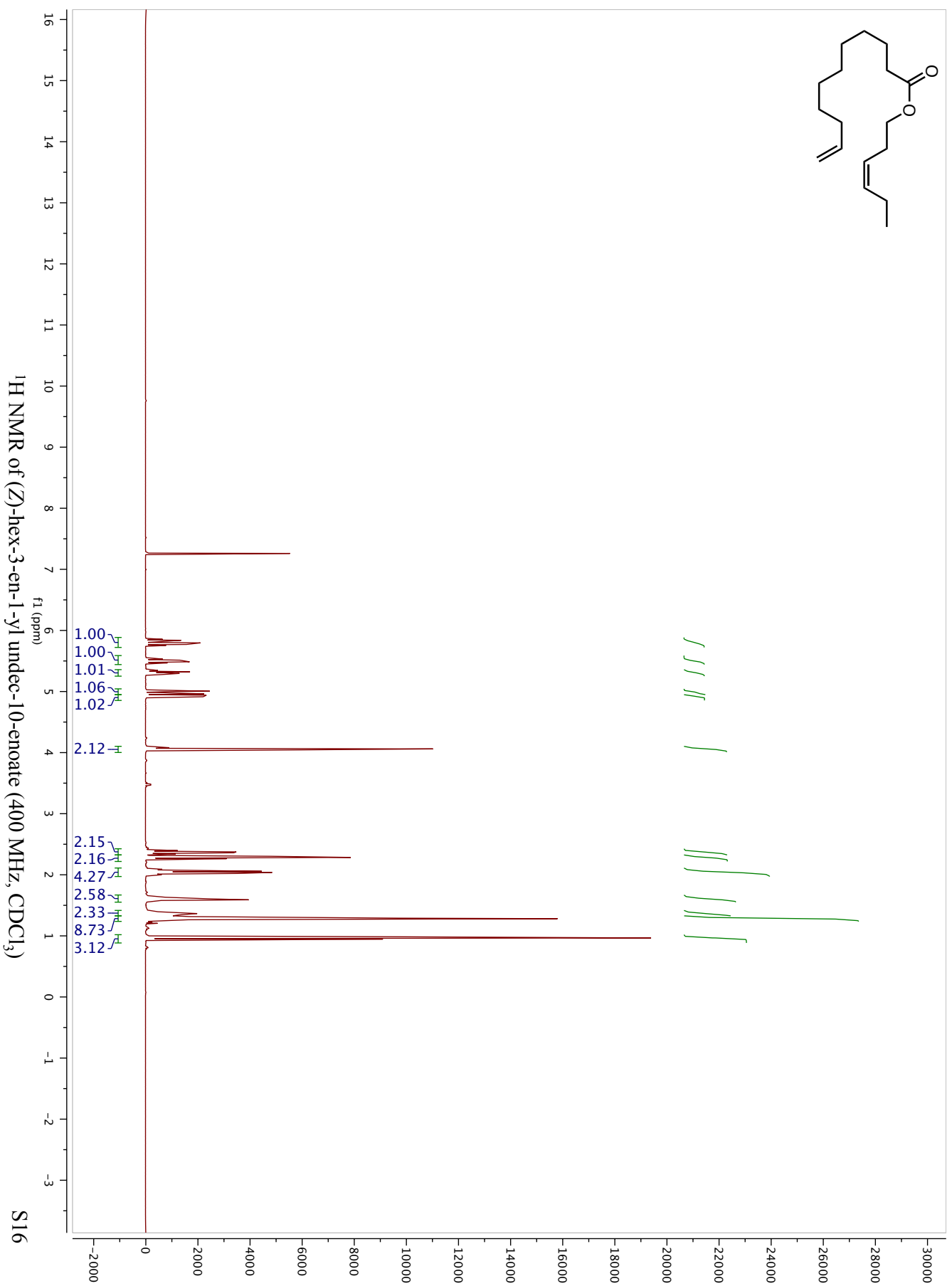
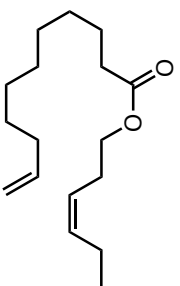


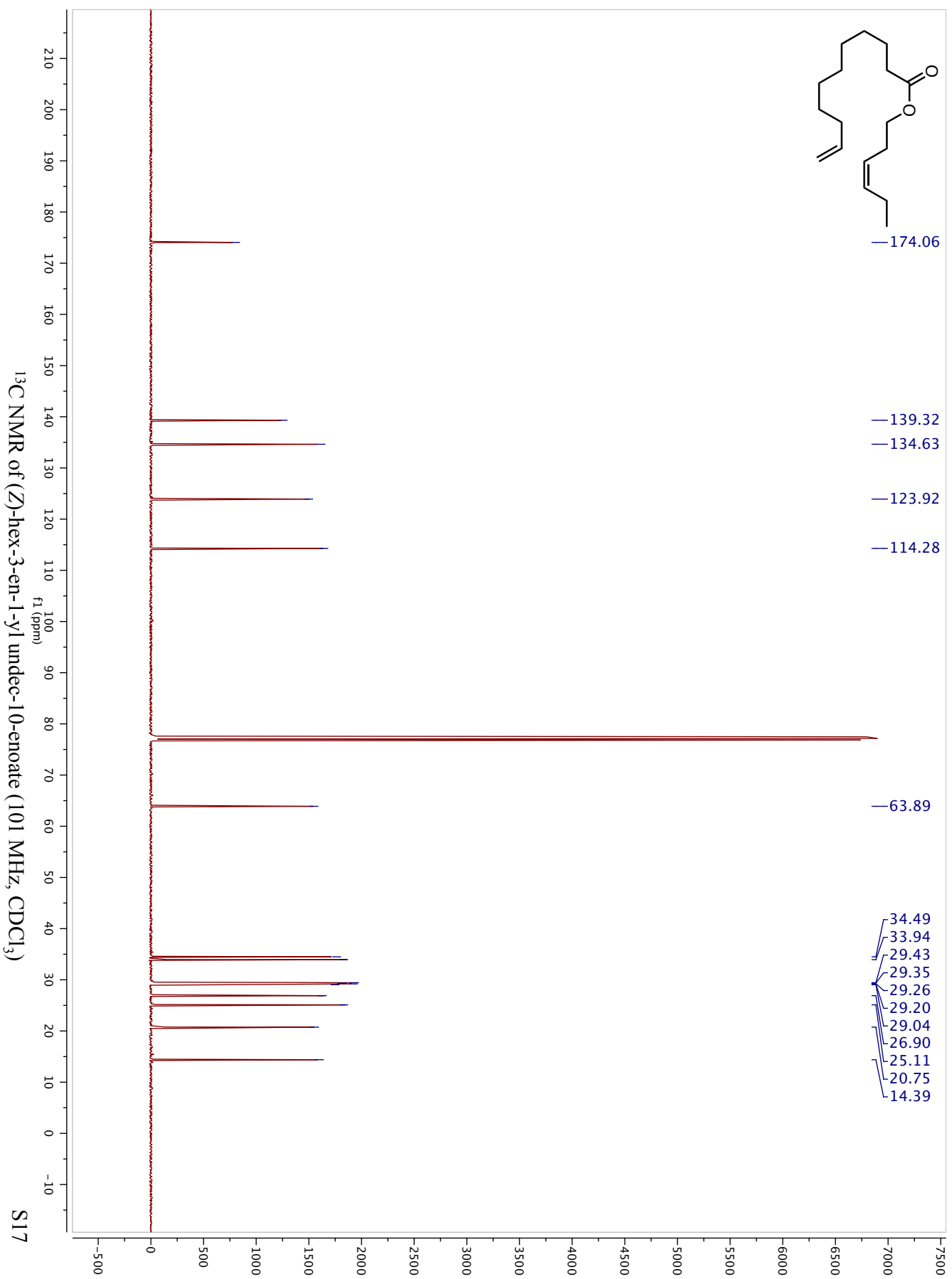
¹³C NMR of (Z)-hex-4-en-1-yl oct-7-enoate (101 MHz, CDCl₃)

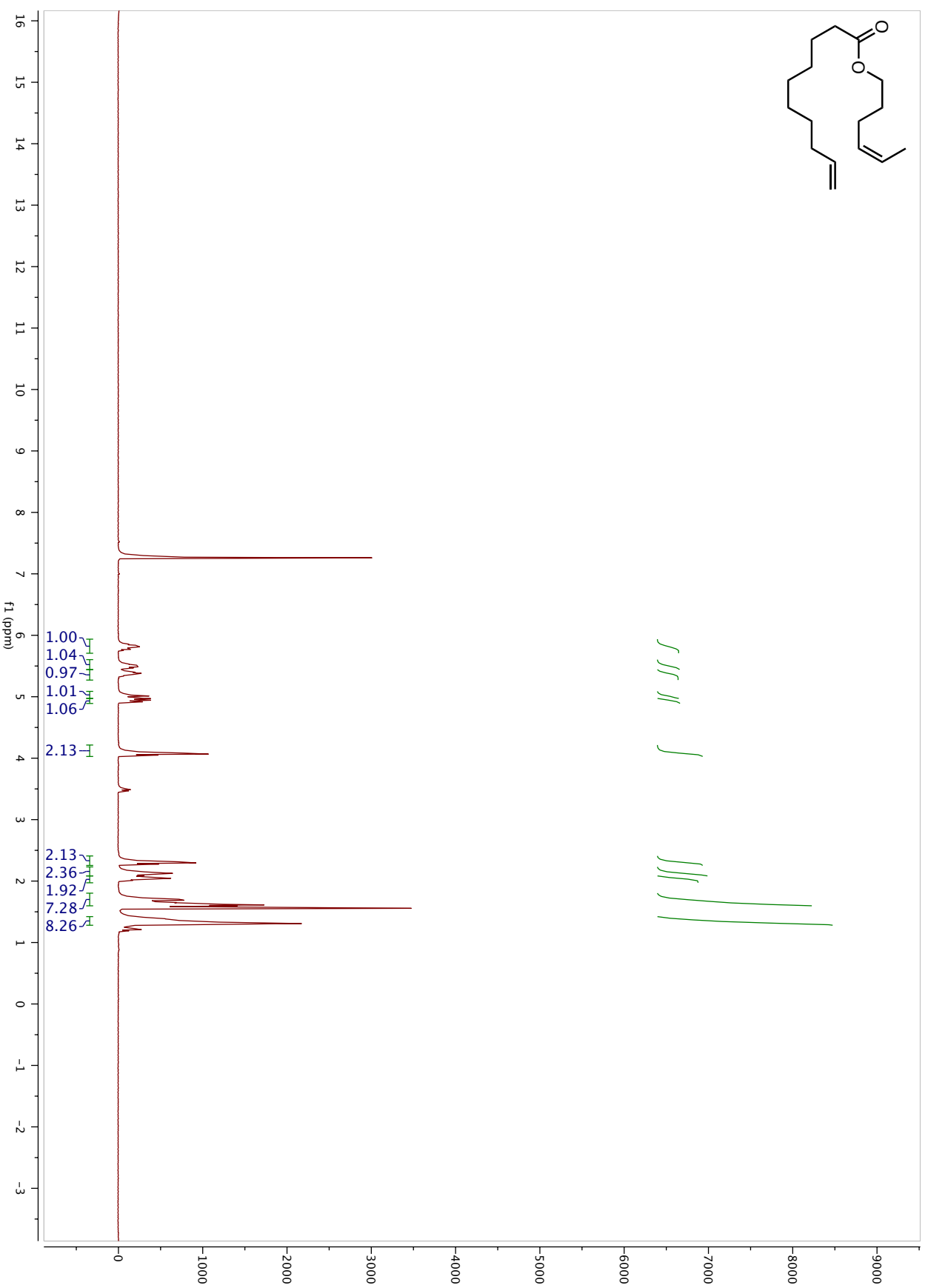
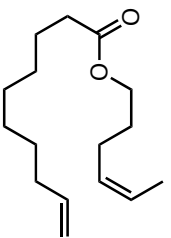


¹H NMR of (Z)-hex-3-en-1-yl dec-9-enoate (400 MHz, CDCl₃)

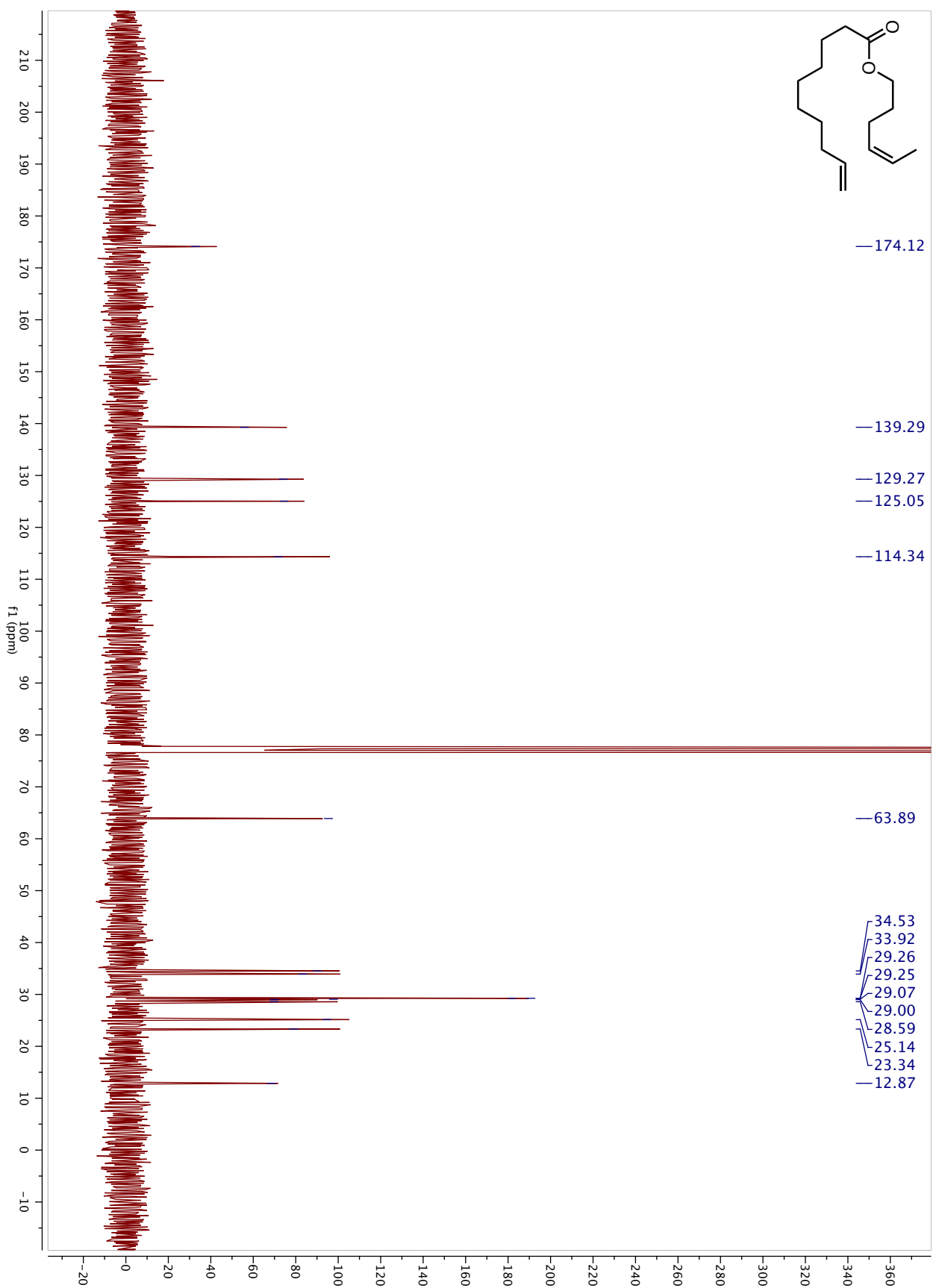
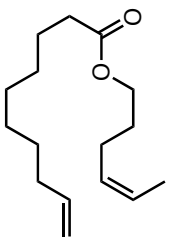




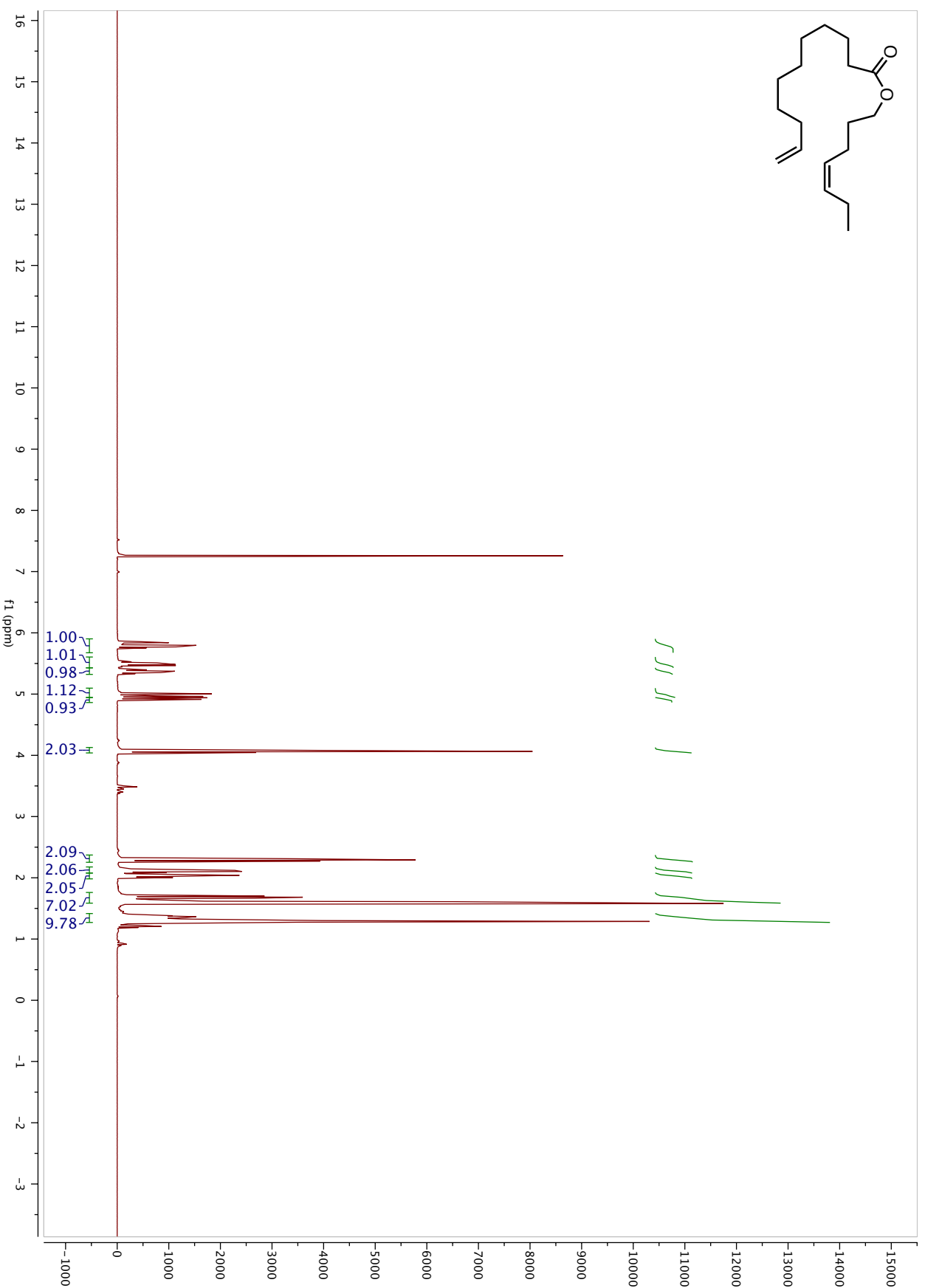
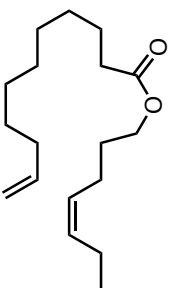




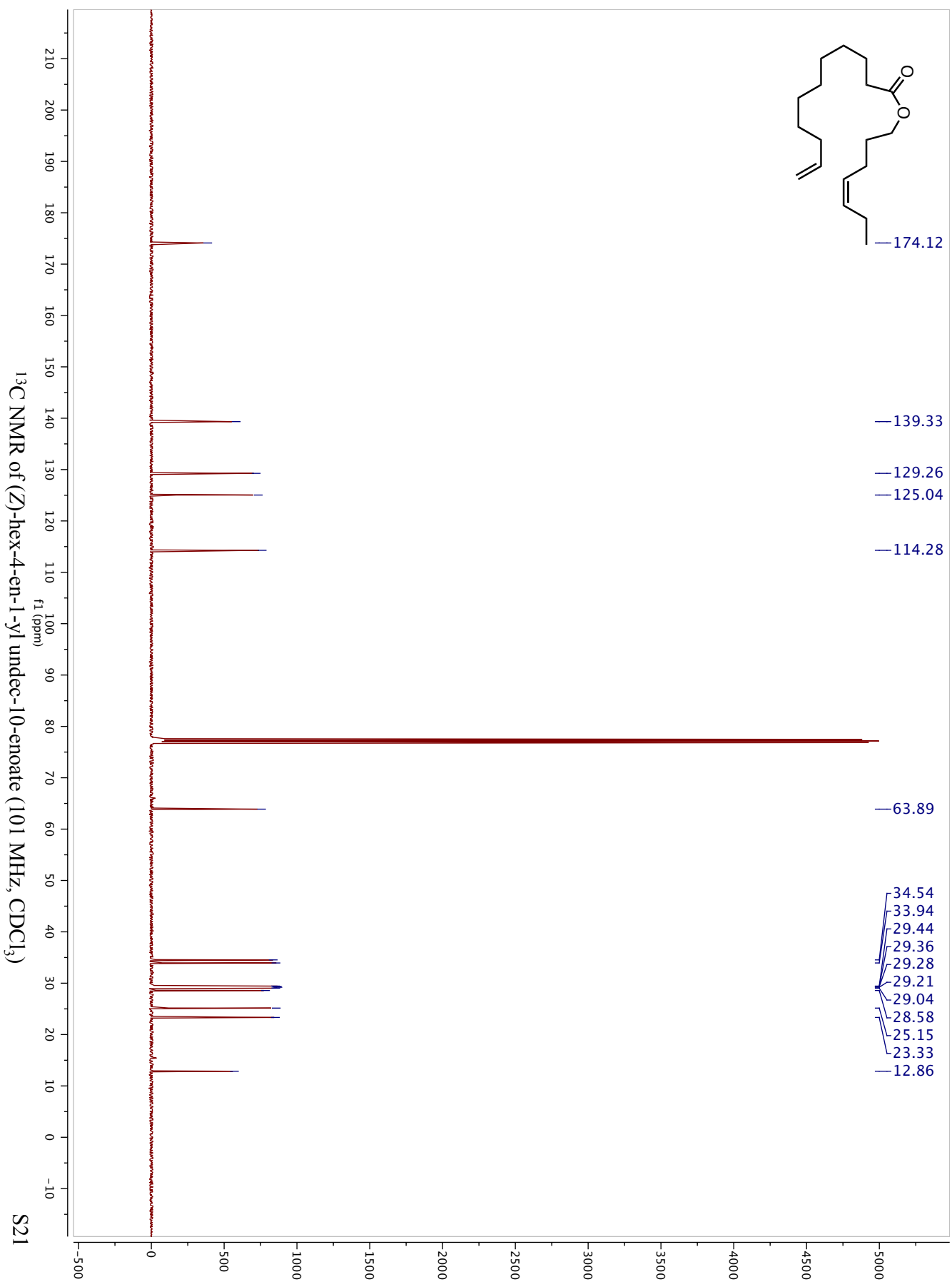
¹H NMR of (Z)-hex-4-en-1-yl dec-9-enoate (400 MHz, CDCl₃)

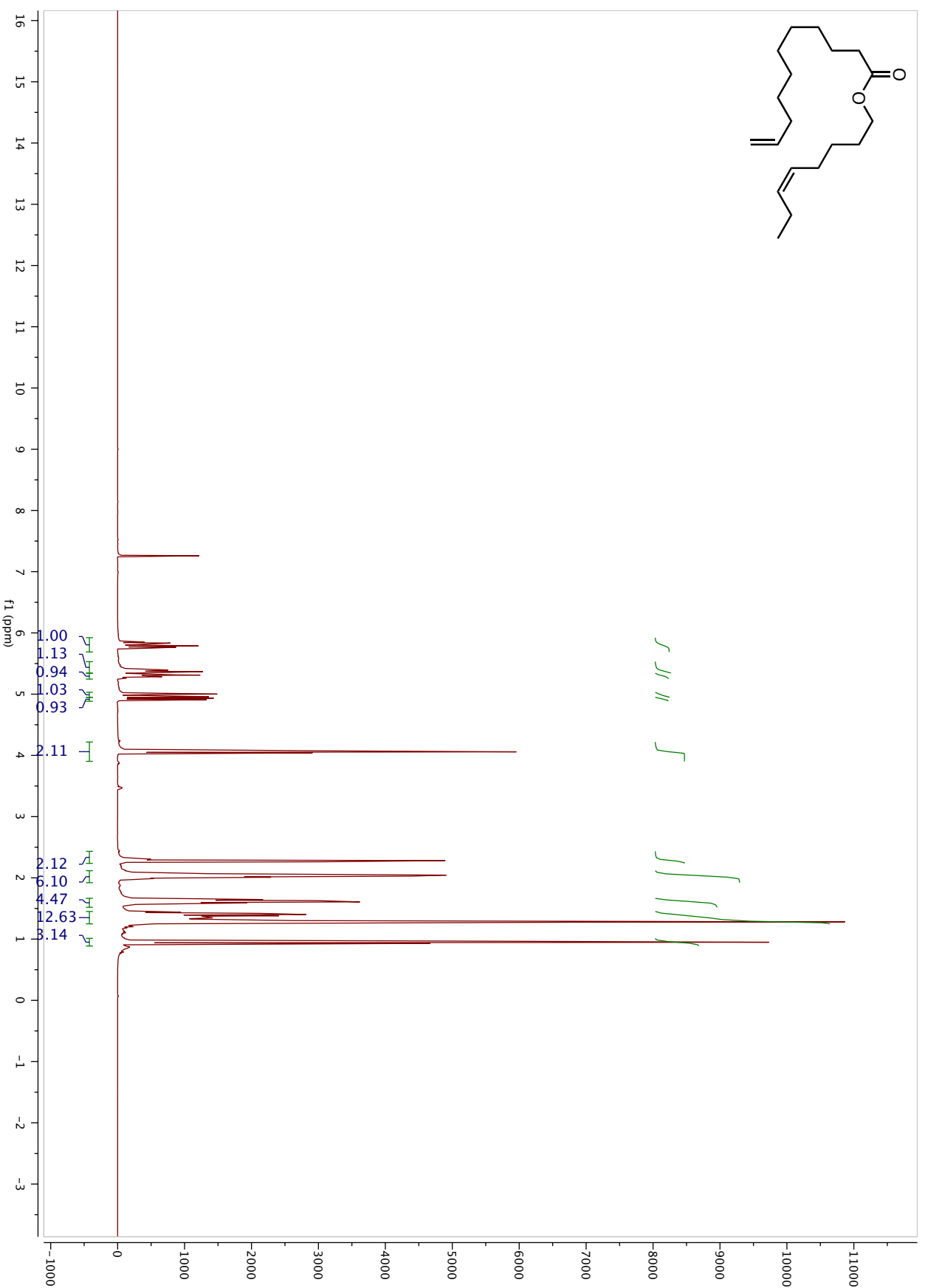
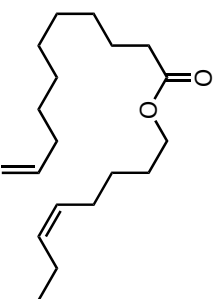


^{13}C NMR of (Z)-hex-4-en-1-yl dec-9-enoate (101 MHz, CDCl_3)



¹H NMR of (Z)-hex-4-en-1-yl undec-10-enoate (400 MHz, CDCl₃)

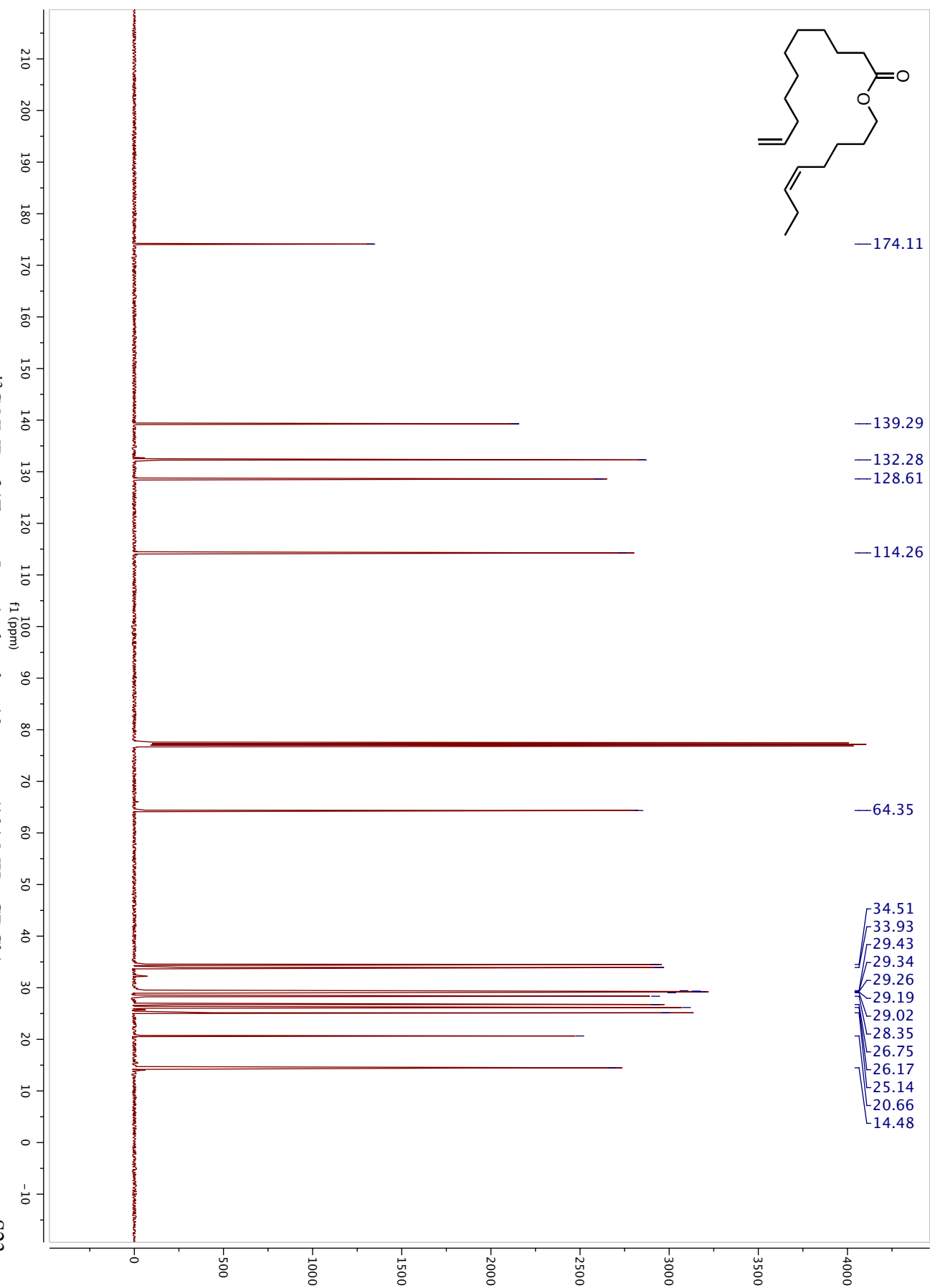


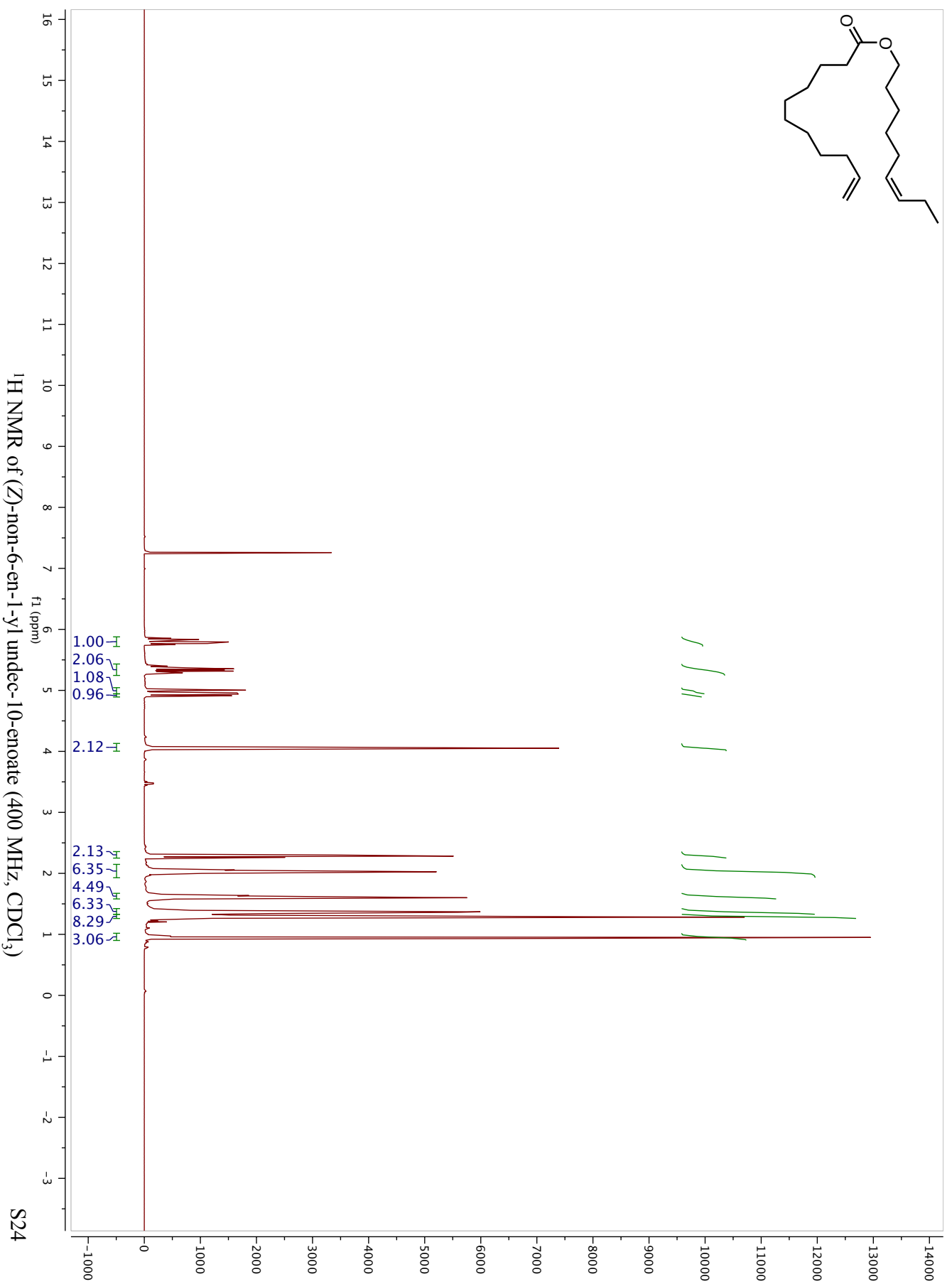
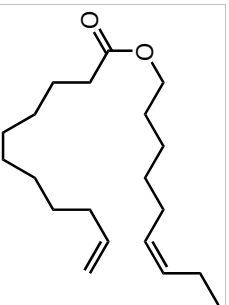


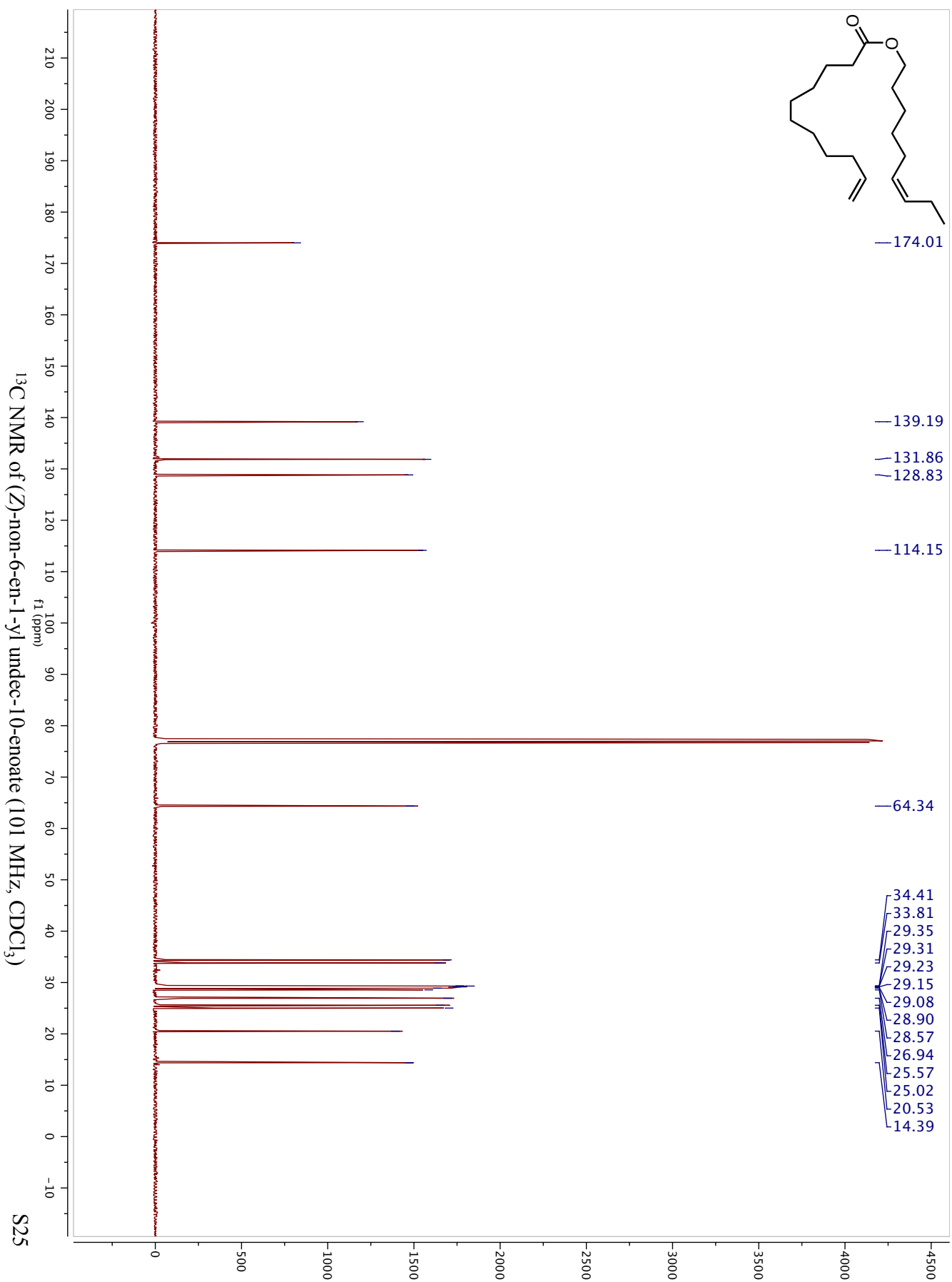
¹H NMR of (Z)-oct-5-en-1-yl undec-10-enoate (400 MHz, CDCl₃)

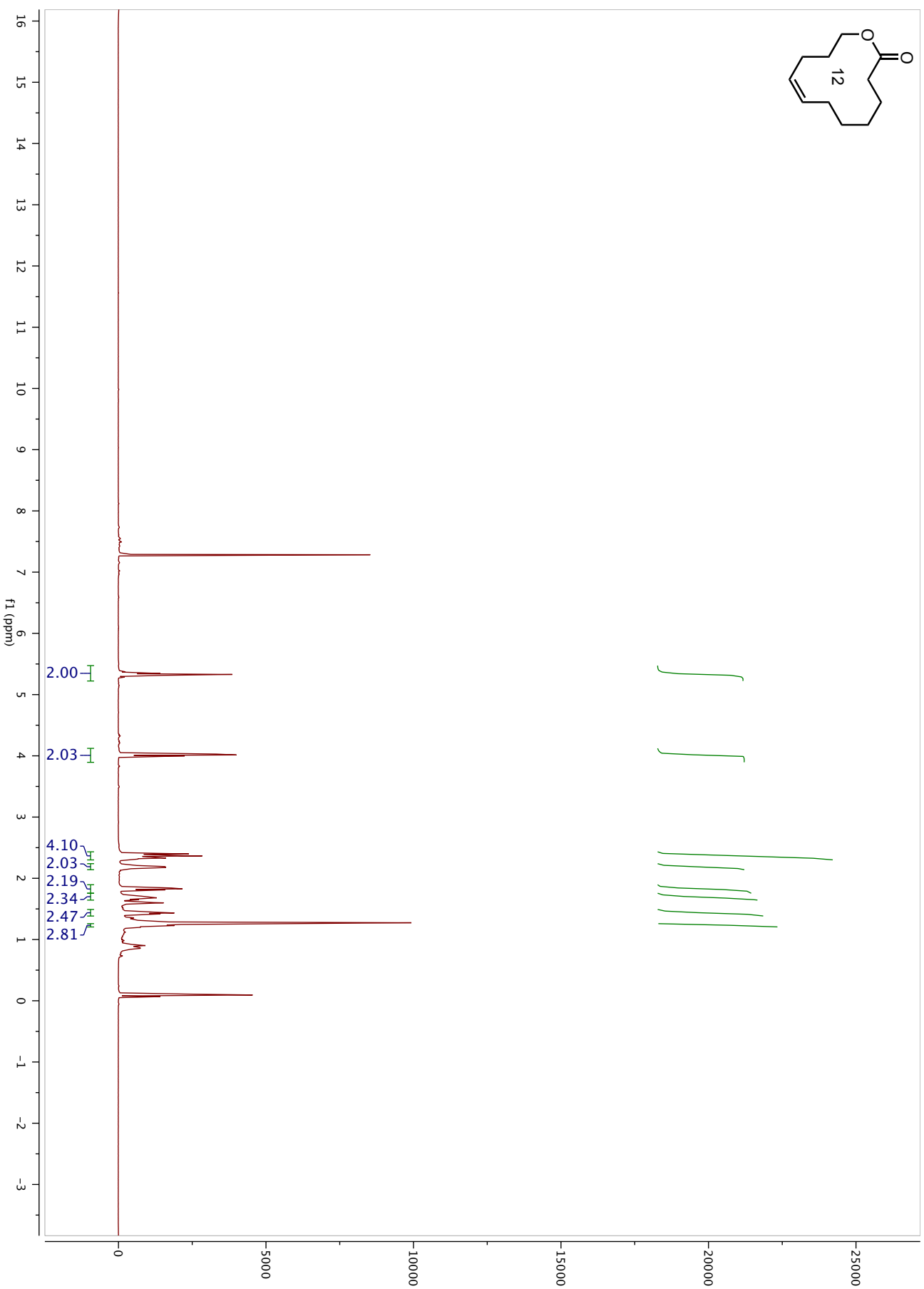
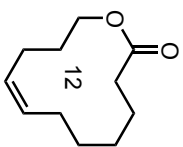
^{13}C NMR of (Z)-oct-5-en-1-yl undec-10-enoate (101 MHz, CDCl_3)

S23

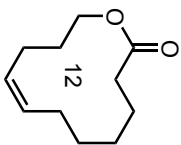








¹H NMR of (Z)-oxacyclododec-8-en-2-one (400 MHz, CDCl₃)



—174.18

—131.37

—128.57

—62.31

35.73

29.86

26.80

26.30

25.14

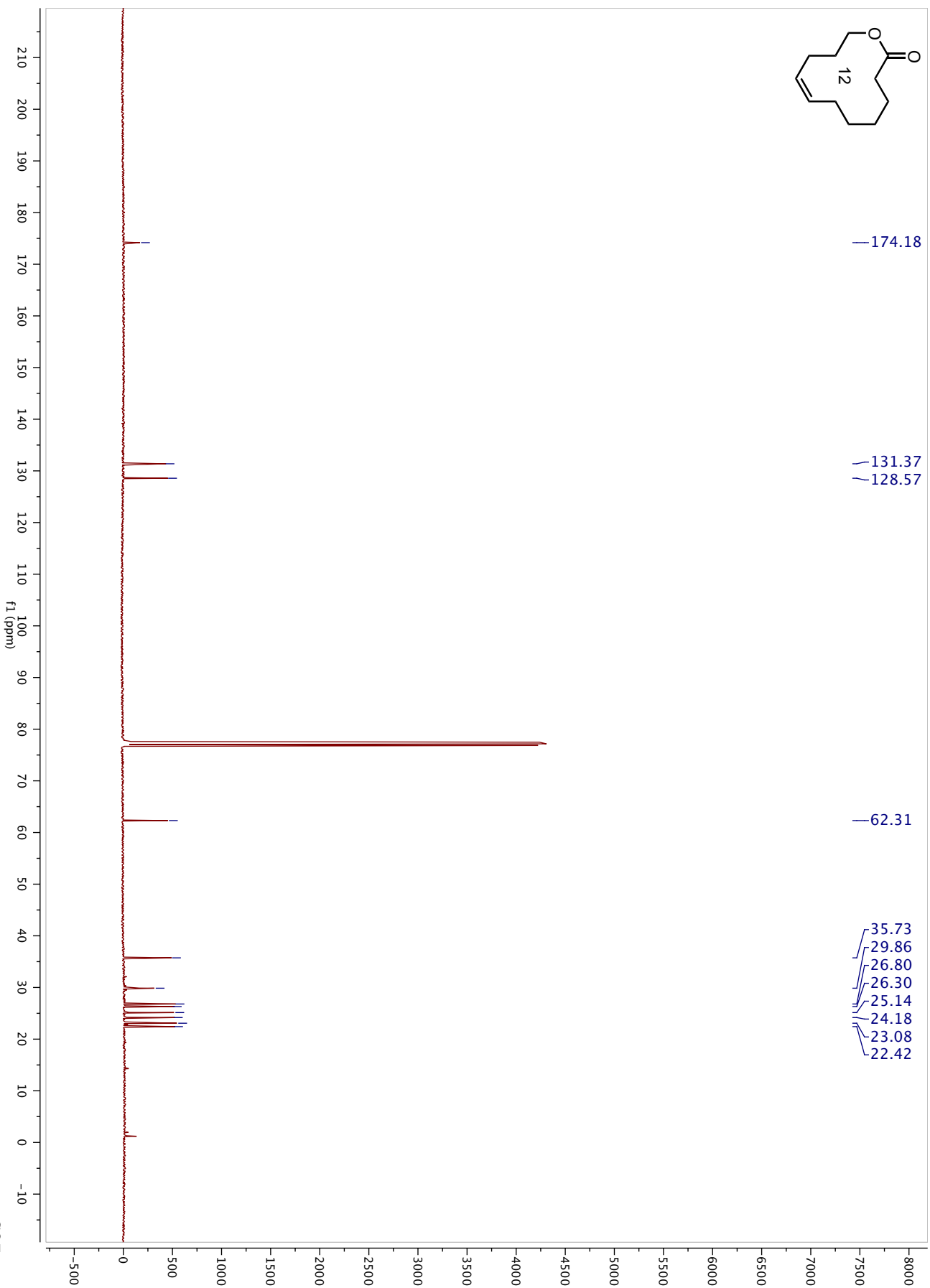
24.18

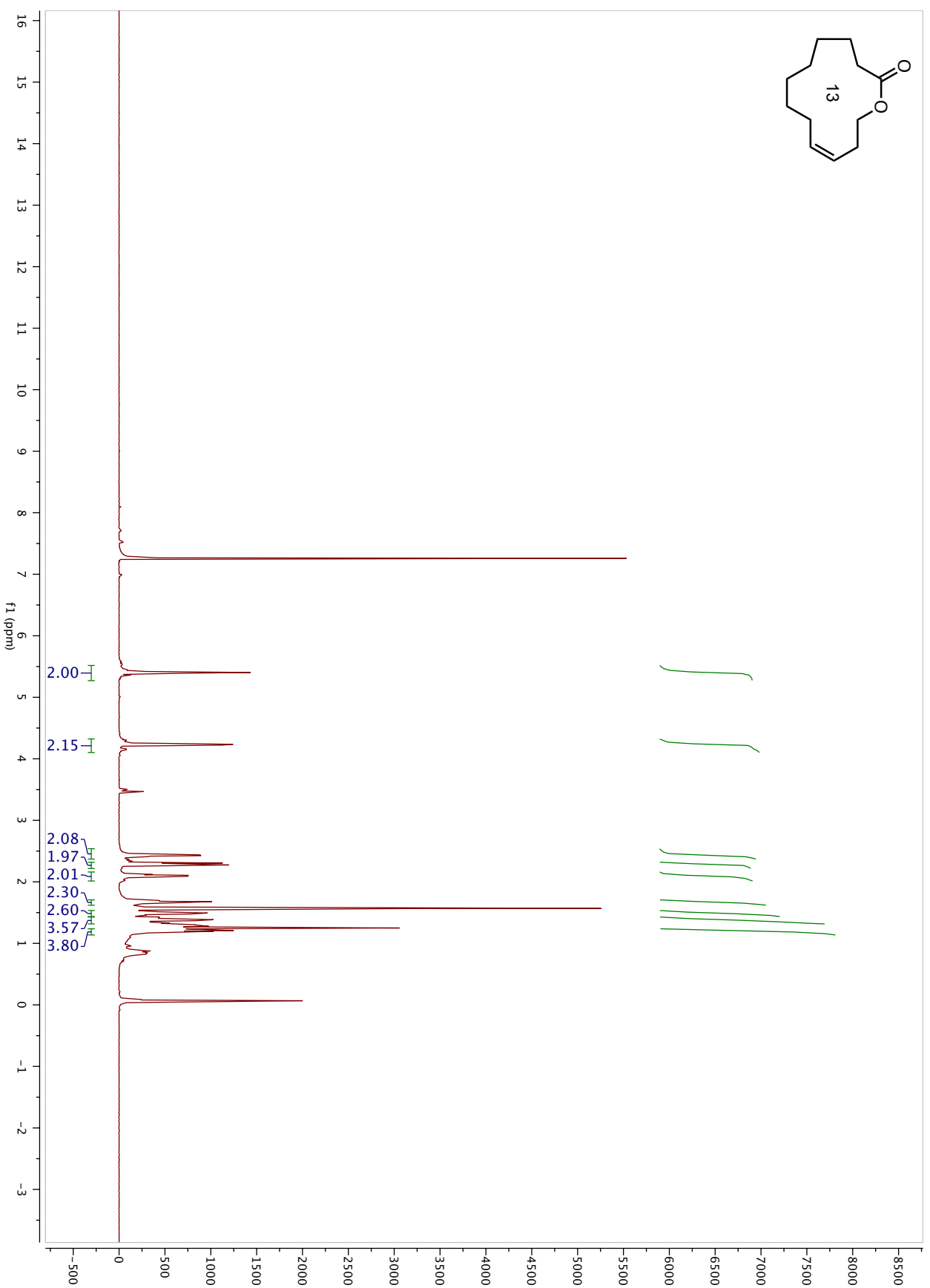
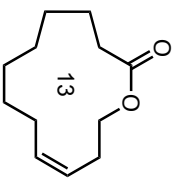
23.08

22.42

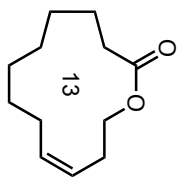
^{13}C NMR of (*Z*)-oxacyclododec-8-en-2-one (101 MHz, CDCl_3)

S27





^1H NMR of (Z)-oxacyclotridec-10-en-2-one (400 MHz , CDCl_3)



—174.89

—132.41

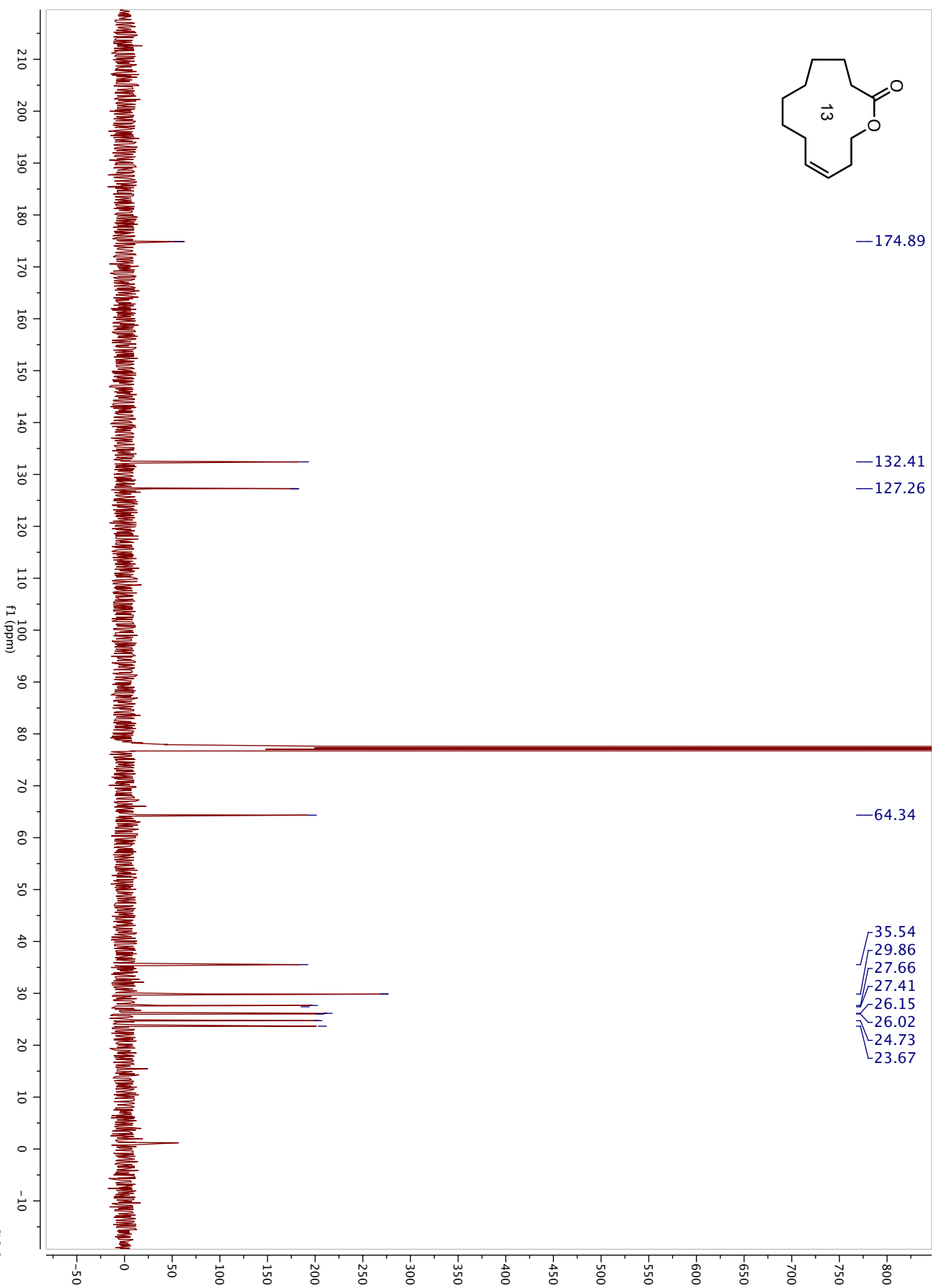
—127.26

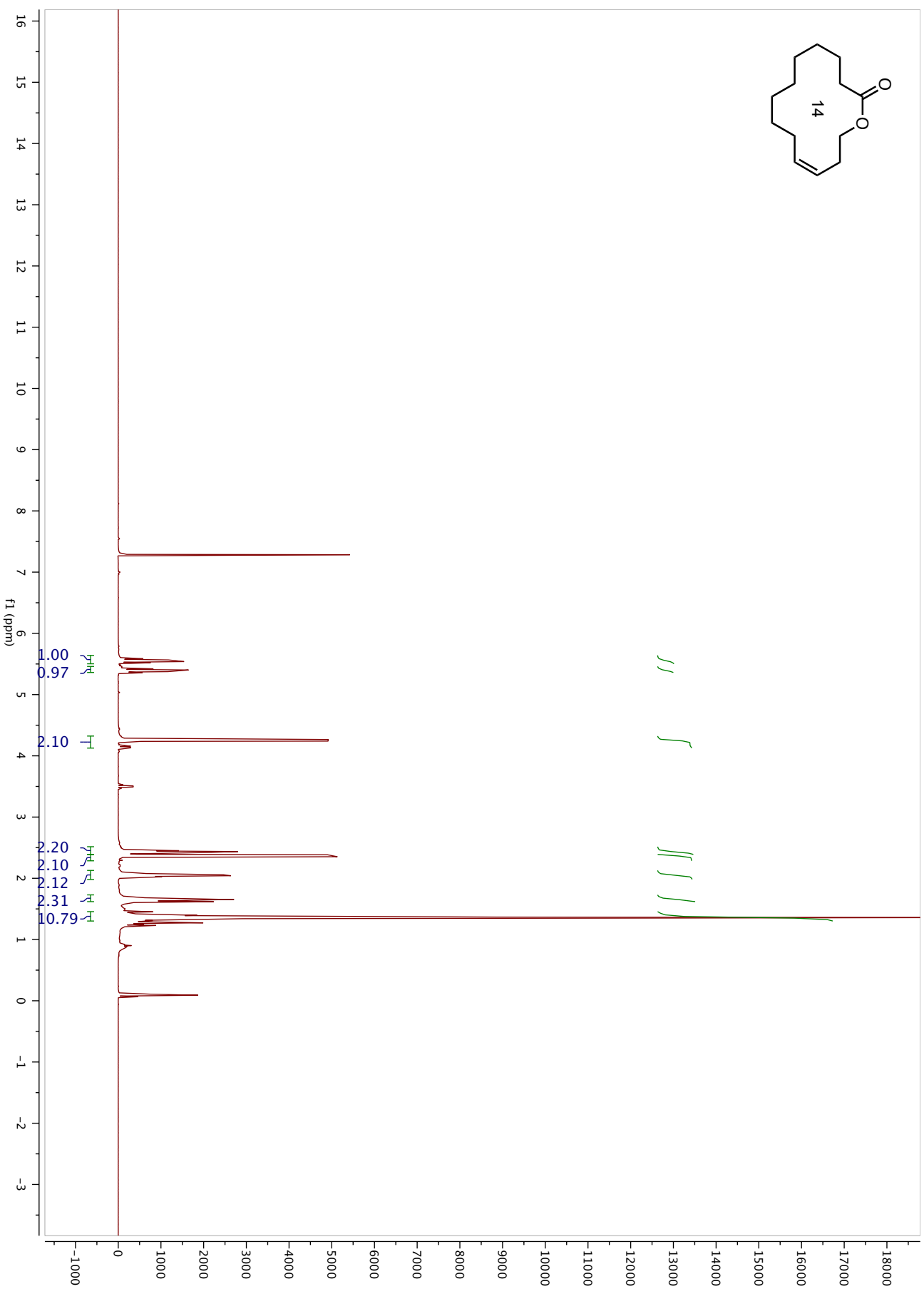
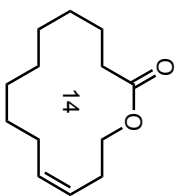
—64.34

35.54
29.86
27.66
27.41
26.15
26.02
24.73
23.67

^{13}C NMR of (Z)-oxacyclotridec-10-en-2-one (101 MHz, CDCl_3)

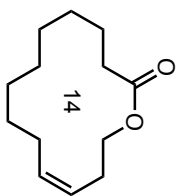
S29





¹H NMR of (*Z*)-oxacyclotetradec-11-en-2-one (400 MHz, CDCl₃)

S30



—174.13

—132.47

—127.22

—63.89

33.46

27.85

27.65

26.25

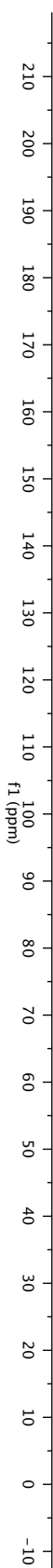
26.14

25.67

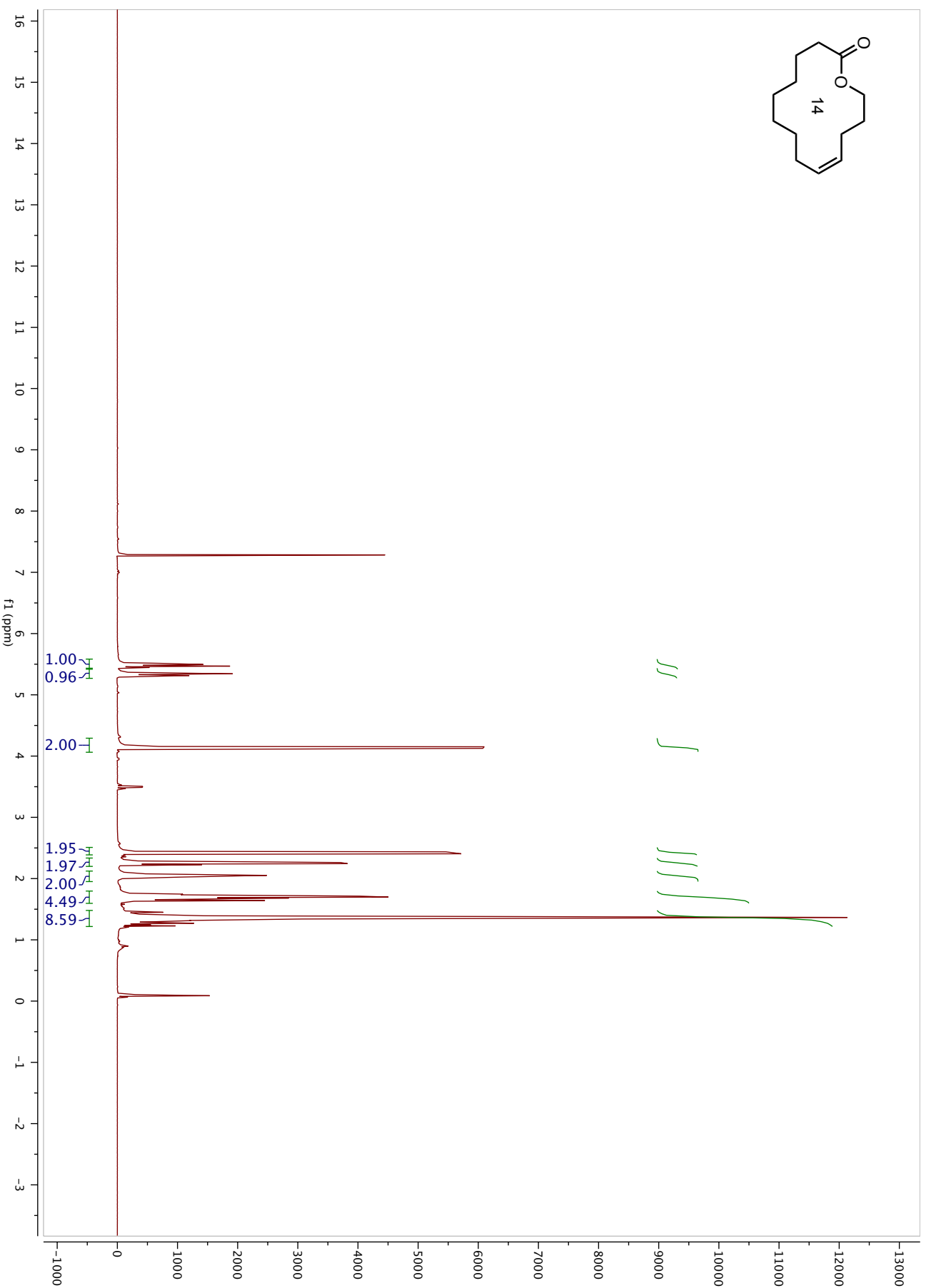
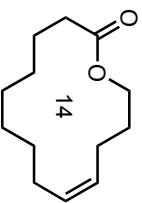
25.56

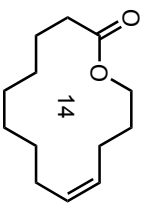
25.34

23.65



^{13}C NMR of (*Z*)-oxacyclotetradec-1-en-2-one (101 MHz, CDCl_3)



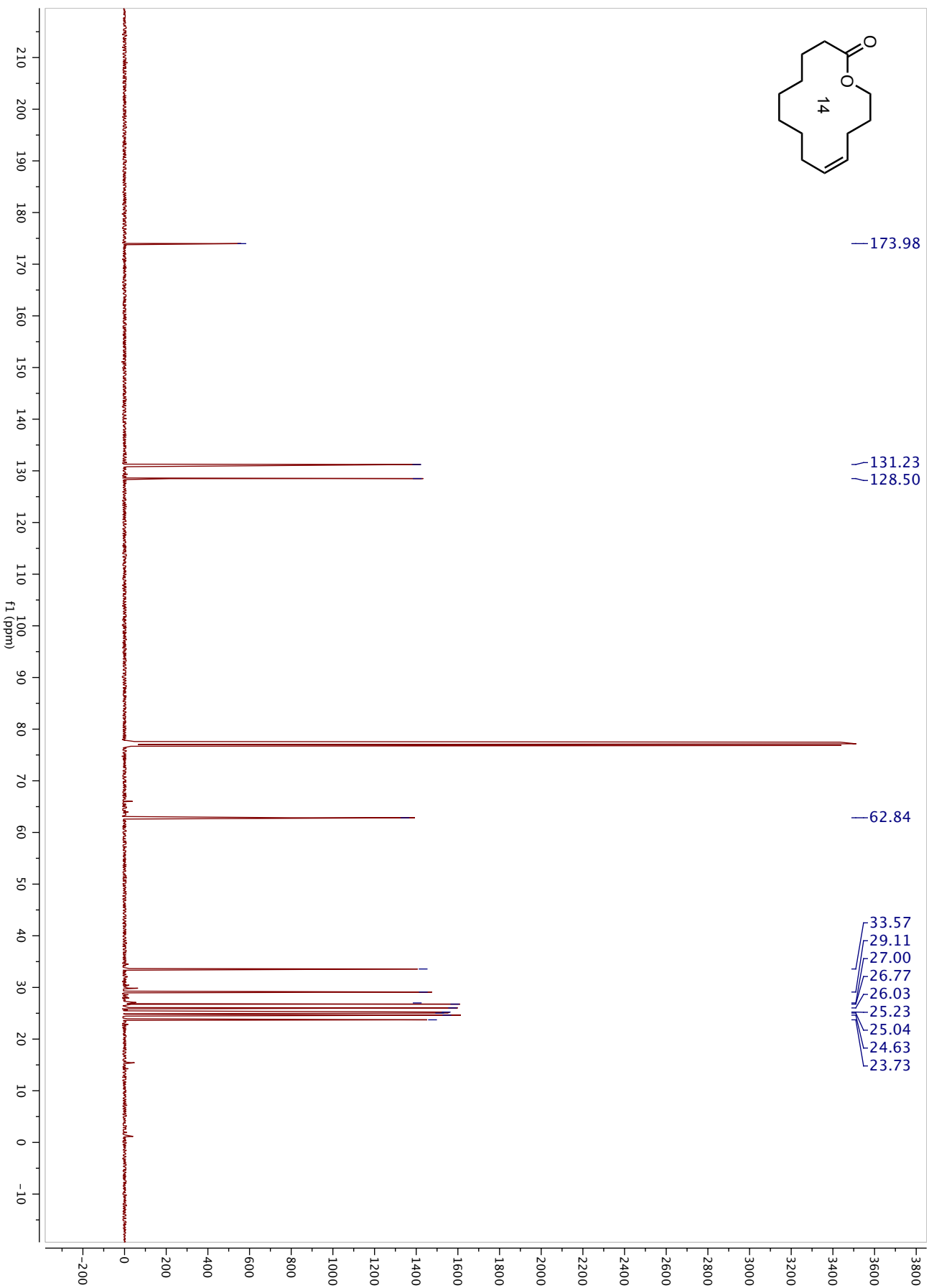


—173.98

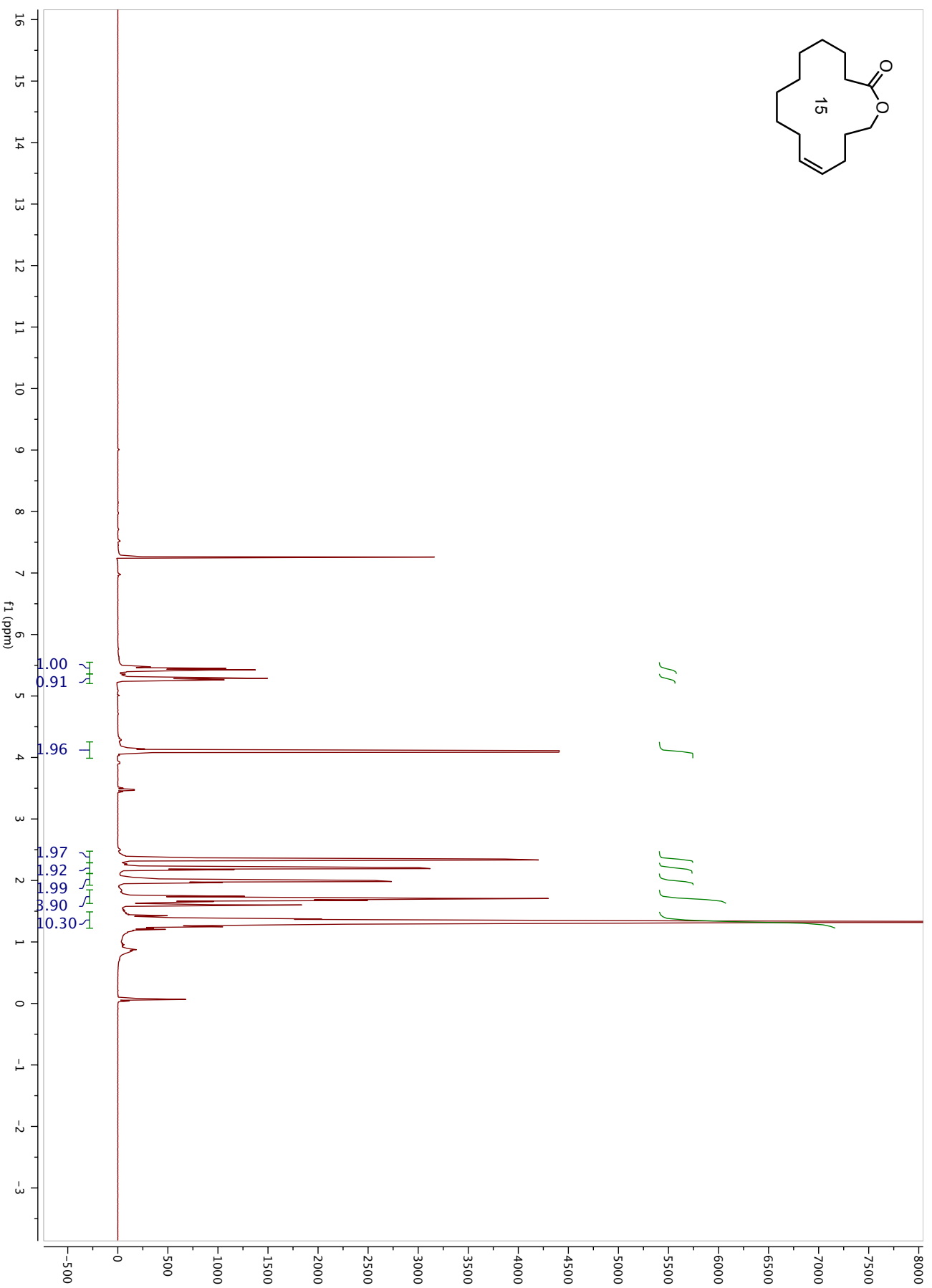
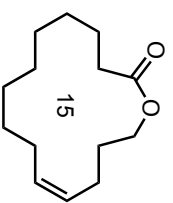
—131.23
—128.50

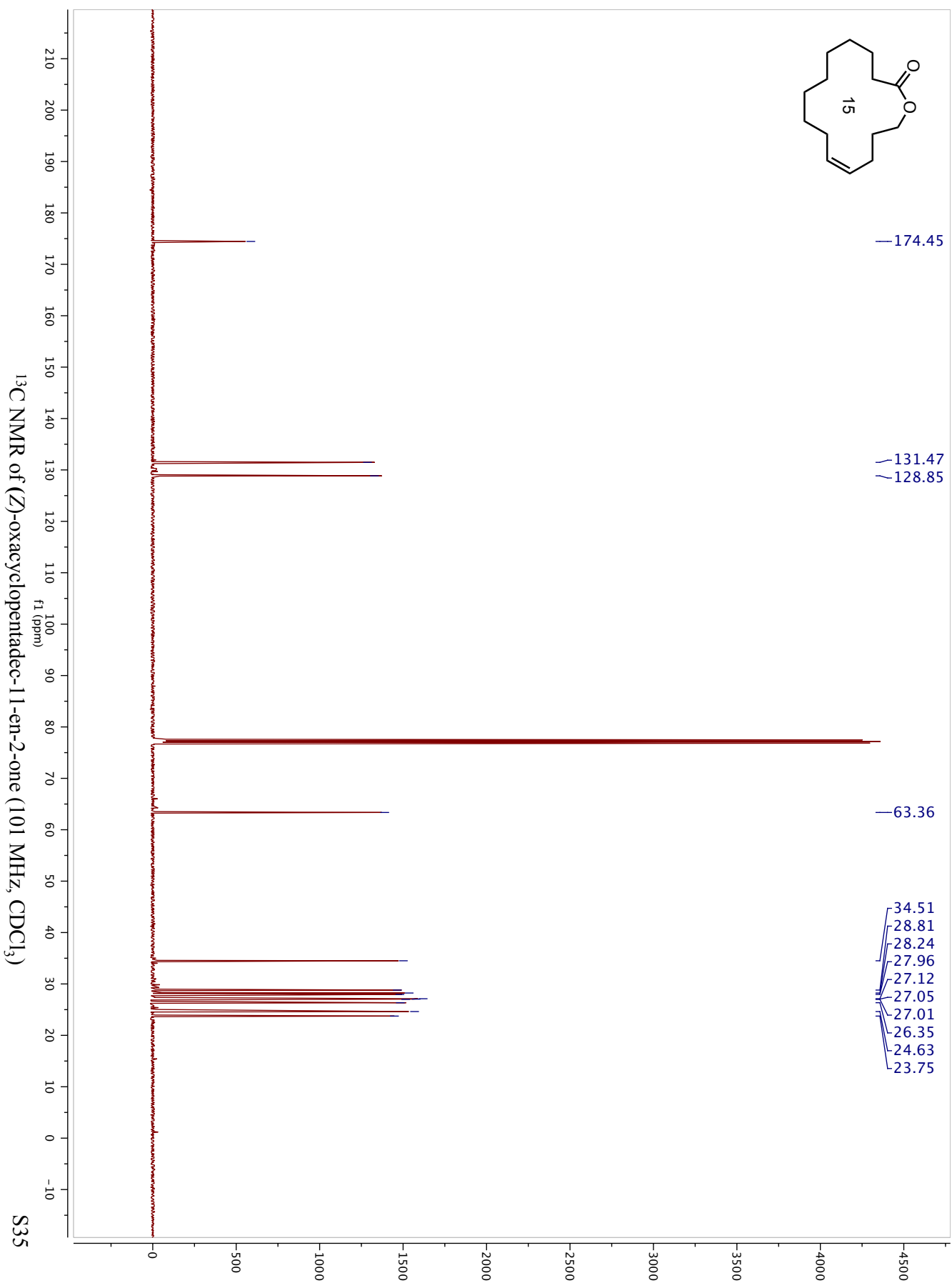
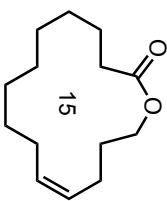
—62.84

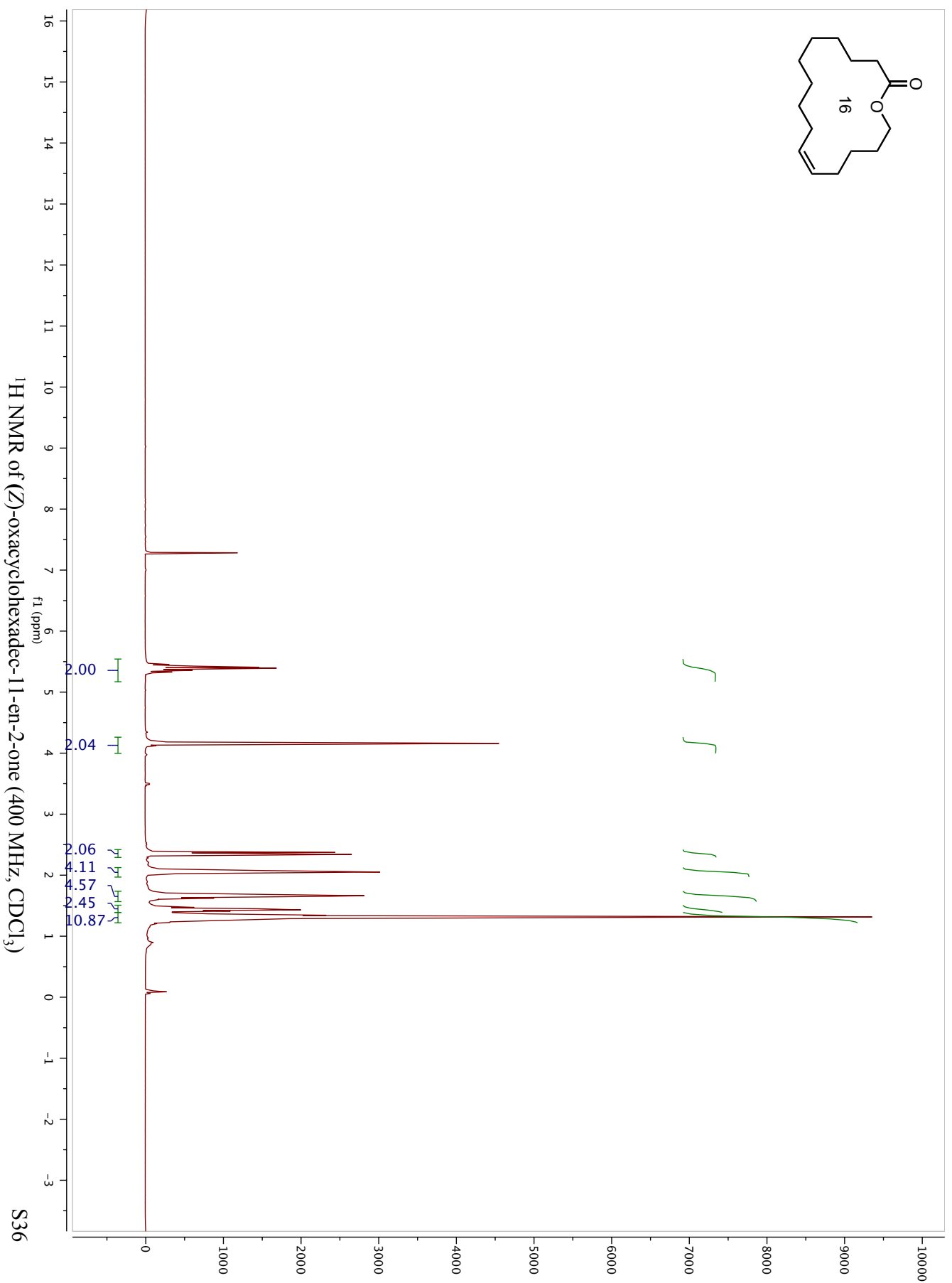
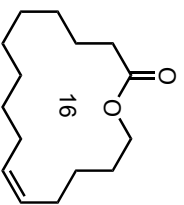
33.57
29.11
27.00
26.77
26.03
25.23
25.04
24.63
23.73

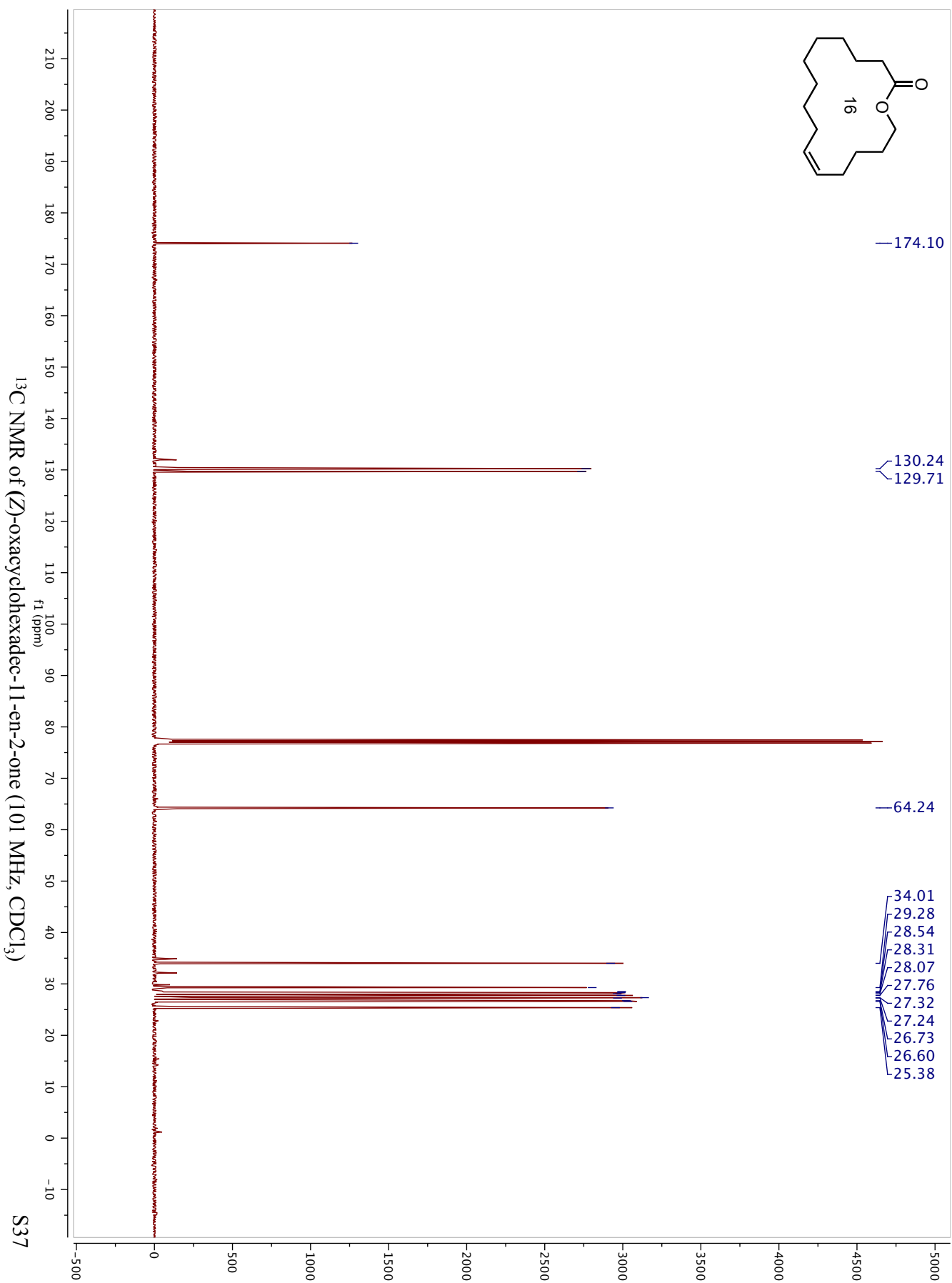
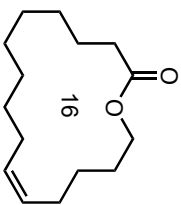


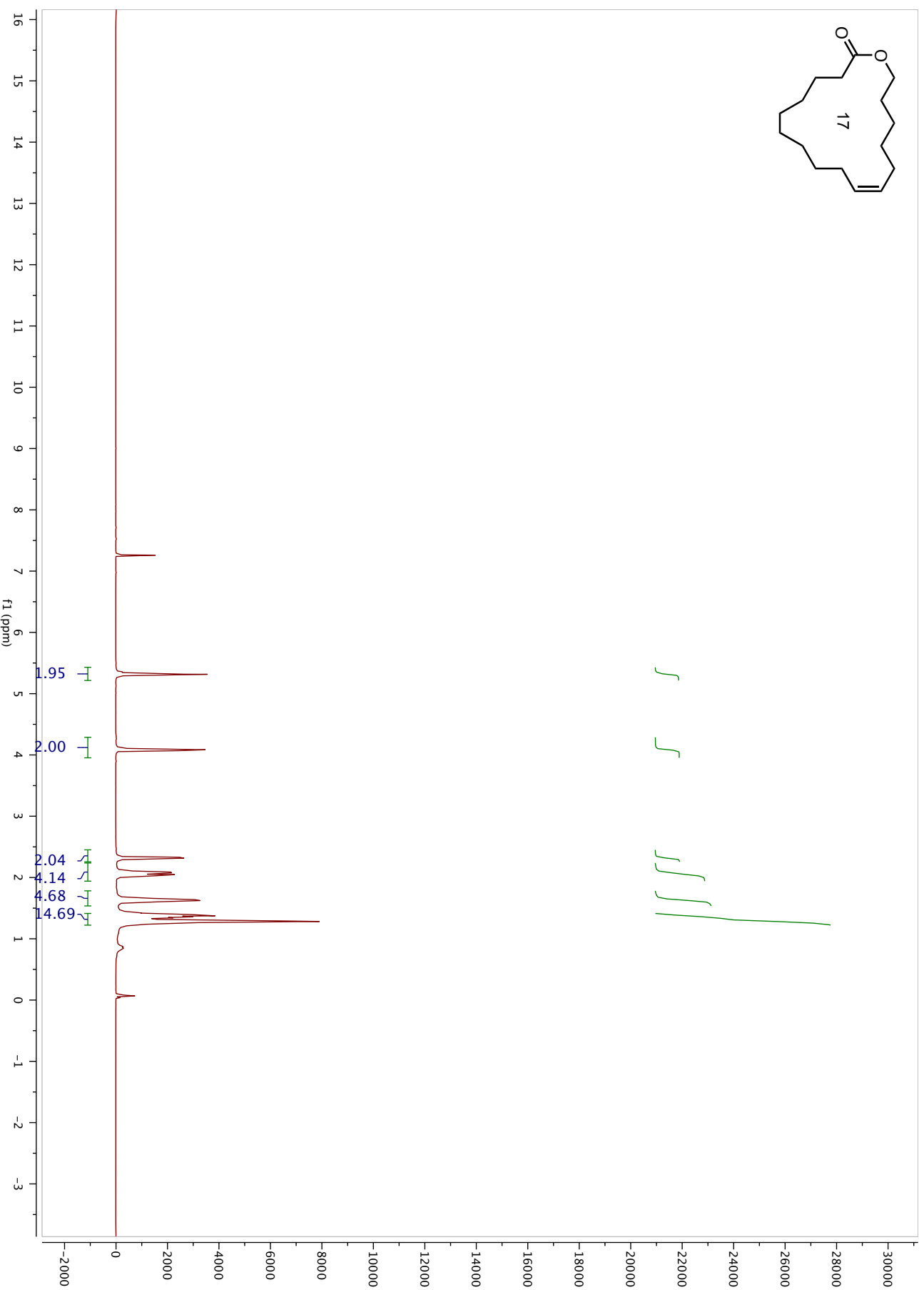
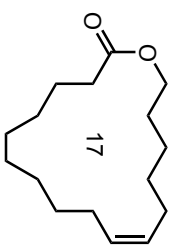
^{13}C NMR of (Z)-oxacyclotetradec-10-en-2-one (101 MHz, CDCl_3)



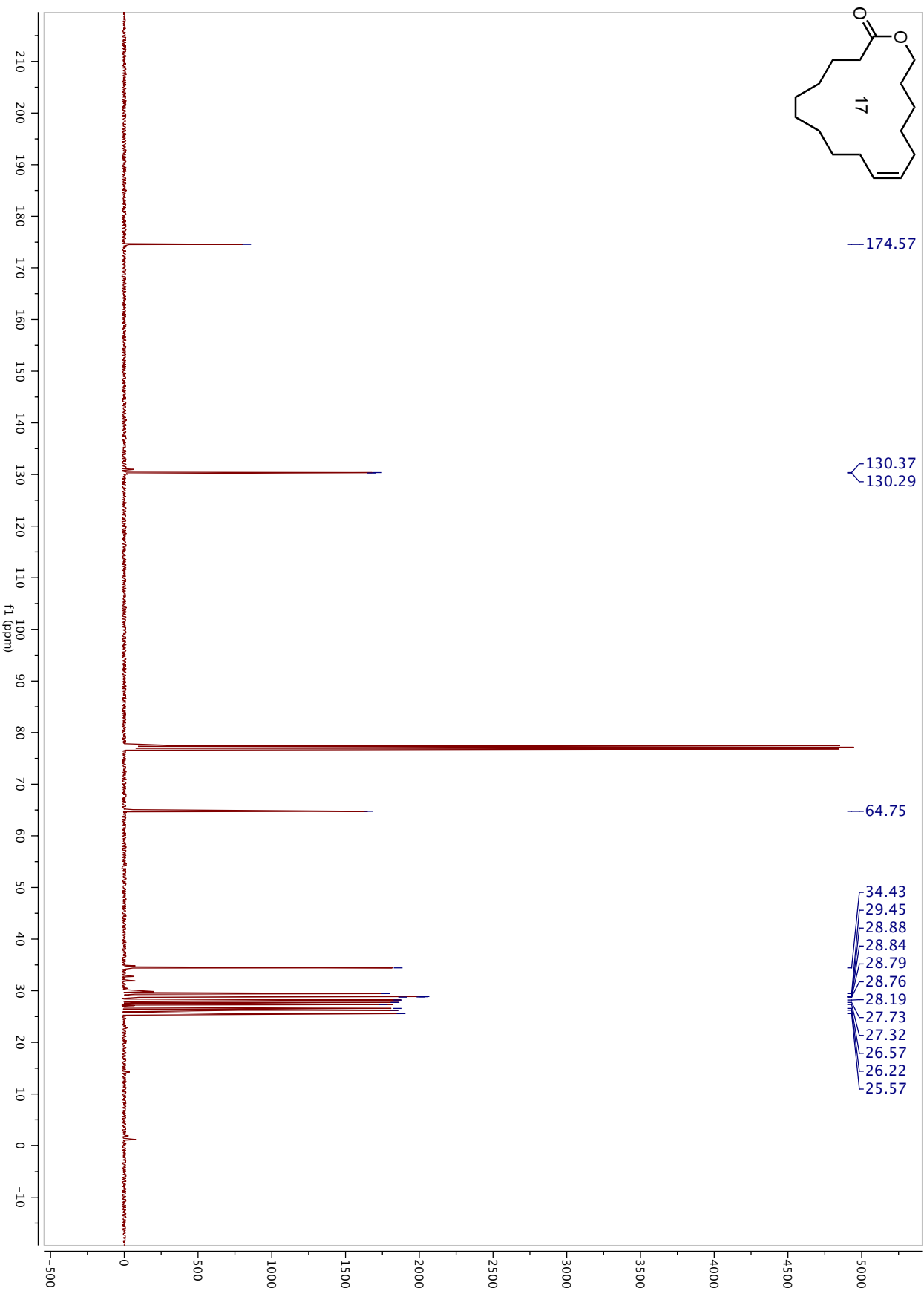
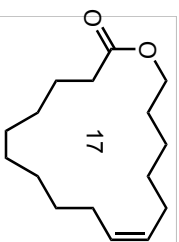




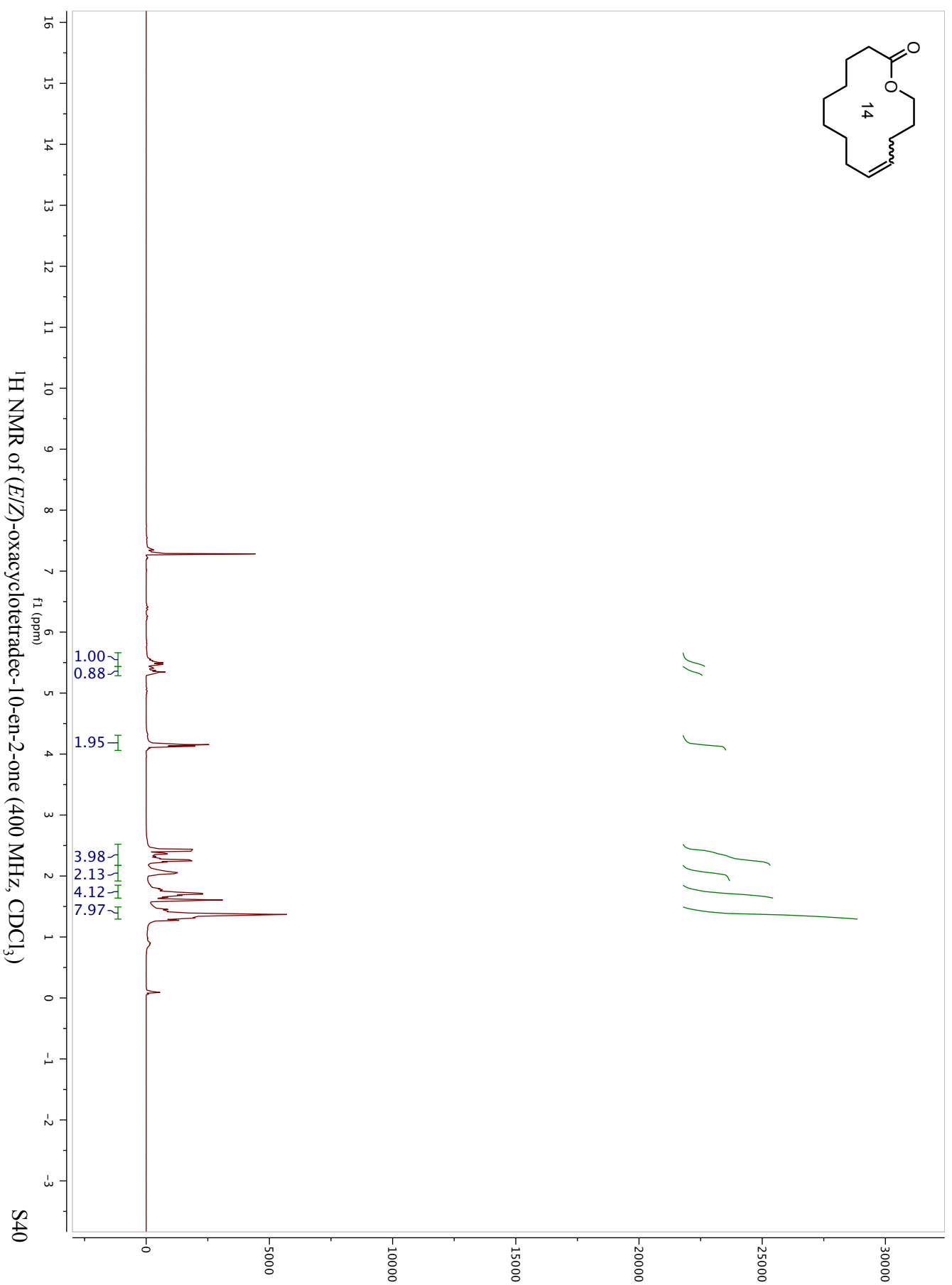
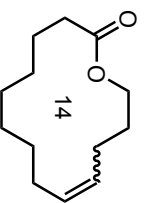


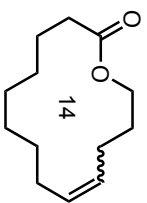


^1H NMR of (Z)-oxacycloheptadec-11-en-2-one (400MHz, CDCl_3)



^{13}C NMR of (Z)-oxacycloheptadec-1-en-2-one (101 MHz, CDCl_3)



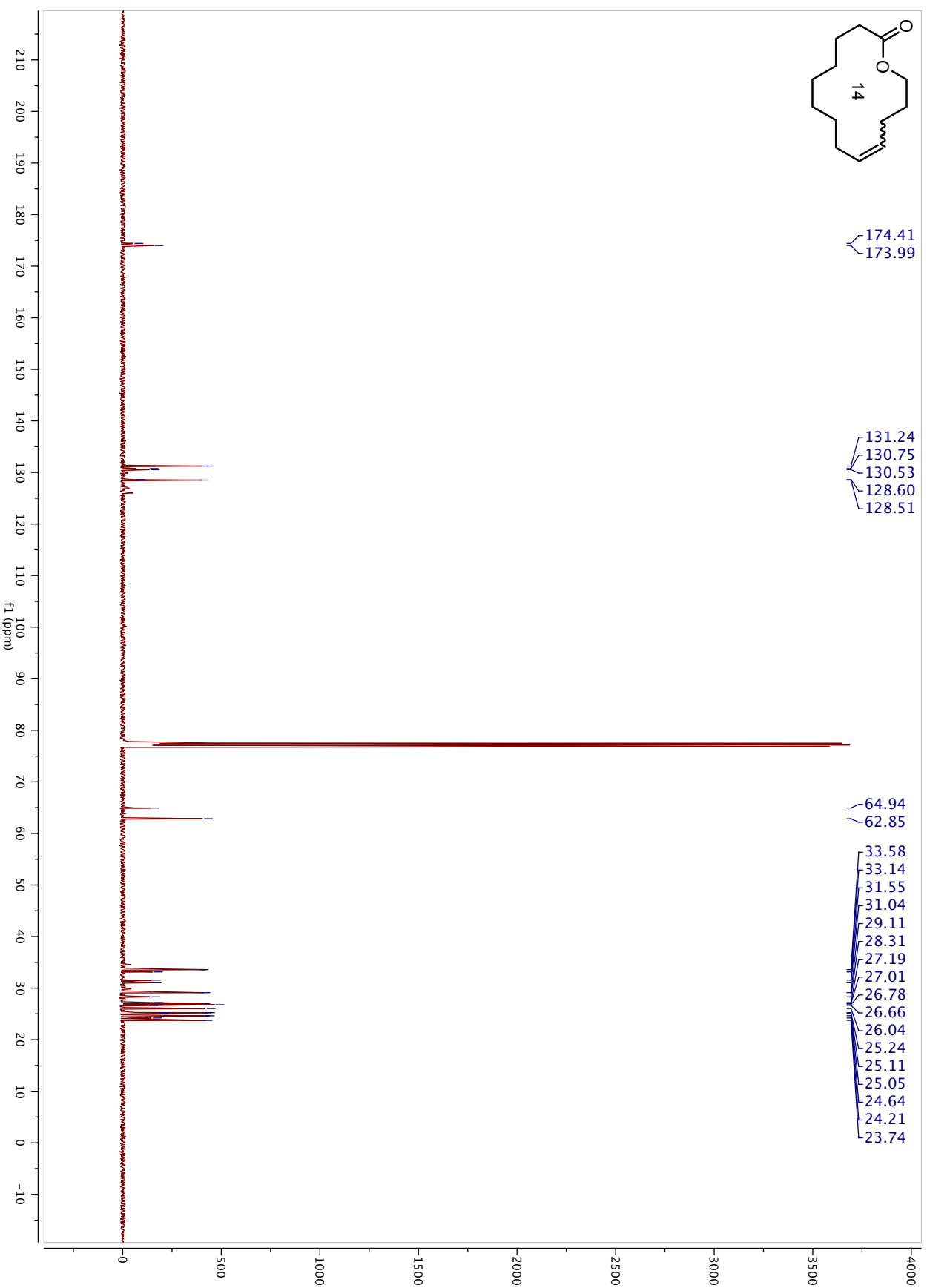


174.41
173.99

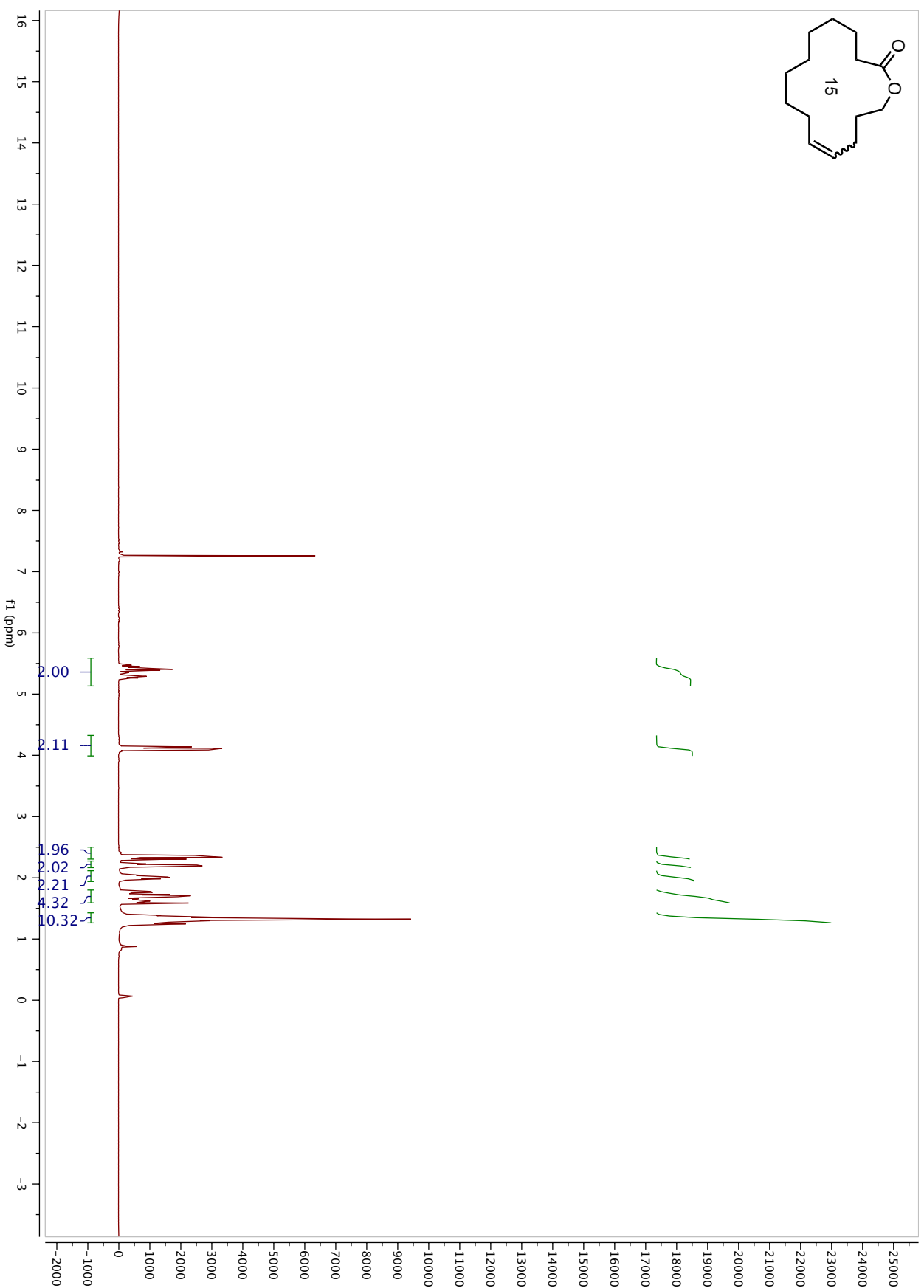
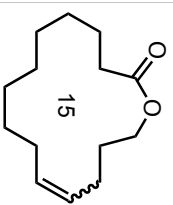
131.24
130.75
130.53
128.60
128.51

64.94
62.85

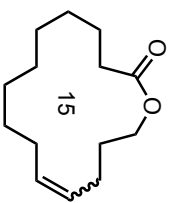
33.58
33.14
31.55
31.04
29.11
28.31
27.19
27.01
26.78
26.66
26.04
25.24
25.11
25.05
24.64
24.21
23.74



^{13}C NMR of (*E/Z*)-oxacyclotetradec-10-en-2-one (101 MHz, CDCl_3)



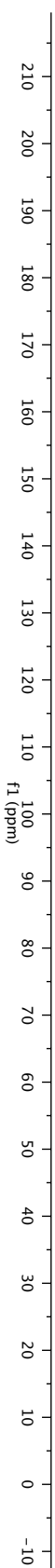
^1H NMR of (E/Z)-oxacyclotetradec-1-en-2-one (400 MHz , CDCl_3)



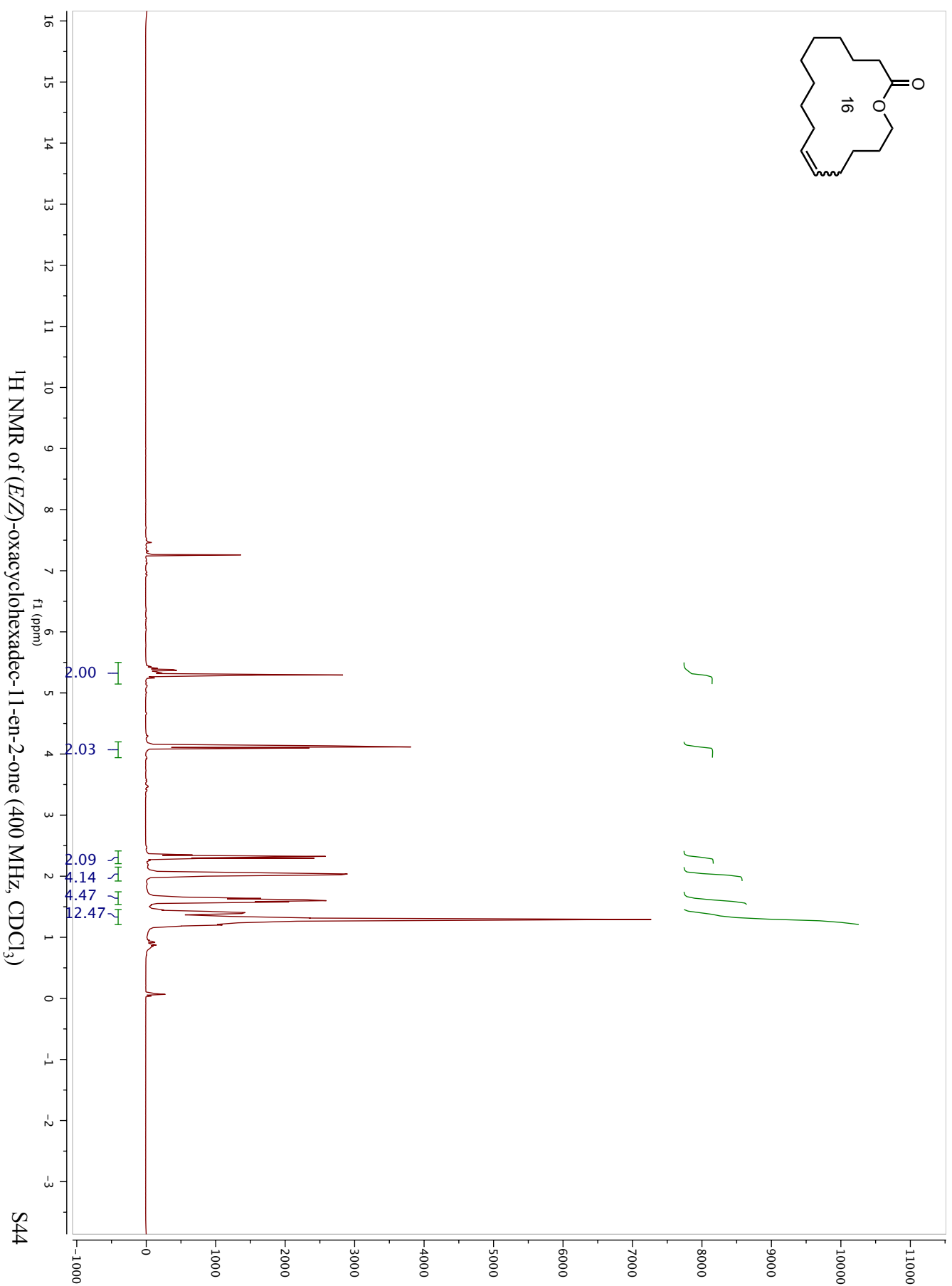
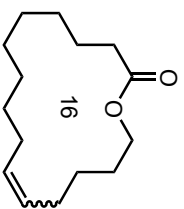
174.48
174.46

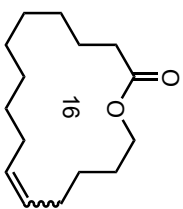
131.97
131.48
129.87
128.85

64.30
63.36
35.01
34.51
31.02
30.32
28.81
28.24
27.96
27.85
27.56
27.13
27.05
27.03
27.01
26.82
26.63
26.35
25.03
24.63
24.57
23.75



^{13}C NMR of (*E/Z*)-oxacyclopentadec-1-en-2-one (101 MHz, CDCl_3)





174.09
174.07

131.95
130.46
130.24
129.71

64.24
64.08
34.89
34.01
32.16
32.12
29.28
28.54
28.47
28.41
28.34
28.31
28.14
28.07
27.76
27.34
27.32
27.25
26.73
26.68
26.61
25.60
25.38
25.30

^{13}C NMR of (*E/Z*)-oxacyclohexadec-11-en-2-one (101 MHz, CDCl_3)

S45

